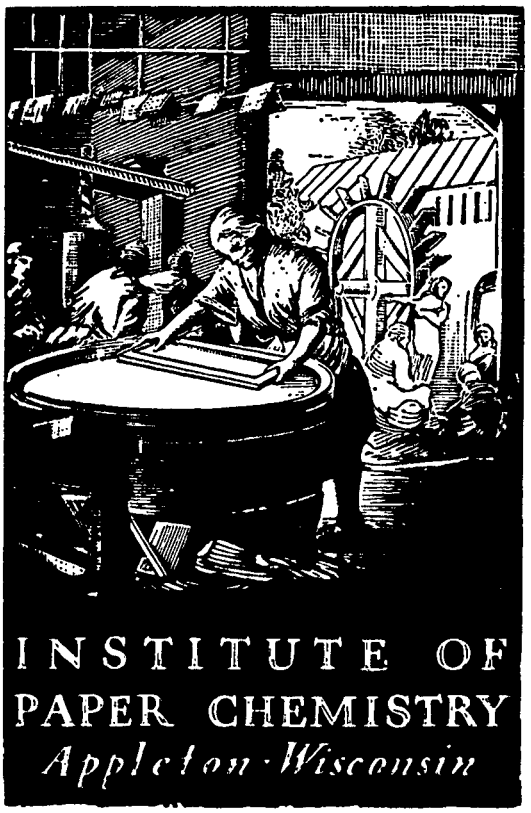

CORROSION RATE MEASUREMENTS IN KRAFT WHITE LIQUOR

Project 3556

Report Two
A Progress Report
to
MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY

May 21, 1984

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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TABLE OF CONTENTS

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ABSTRACT

Corrosion of carbon steel equipment by alkaline sulfide liquors is a serious problem for the kraft pulping industry. An impediment to controlling corrosion in these liquors is an inability to detect periods of high corrosivity in time to take remedial measures. An electrochemical method called the linear polarization measurement has been evaluated as a technique for monitoring corrosion rates in kraft white liquors. Comparisons of linear polarization results and actual weight loss measurements show that, in most cases, linear polarization methods are qualitatively responsive to changes in liquor corrosivity. However, the accuracy of the linear polarization measurement depends on the values assigned to the ratio of two parameters in the corrosion rate equation. Empirically derived values of these parameters are provided in this report for evaluating corrosion rates in several simulated white liquors.

The linear polarization measurement yields erroneous estimates of the corrosion rate when carbon steel is spontaneously passivated, as occurs when the liquor contains high levels of polysulfide species. Oxidation of species present in the liquor occurs on the passive steel surface and this oxidation masquerades as metal dissolution in the linear polarization measurement. Significant errors resulting from liquor oxidation only occur when the rest potential of carbon steel is approximately +100 mV vs. the silver/silver sulfide reference potential. Measurement of the rest potential of carbon steel will provide a warning when errors are likely in linear polarization measurements.

SUMMARY FOR THE NONSPECIALIST

Corrosion of carbon steel components by kraft white liquors leads to premature failure of equipment such as clarifiers, storage tanks, and piping. The corrosion experienced in white liquors fluctuates from day to day, with most of the damage occurring during periods of high corrosivity. Unfortunately, there is no qualified method for detecting these periods of high corrosivity so that remedial measures can be taken before extensive damage occurs. This report describes efforts to qualify an electrochemical method called the linear polarization method as a technique for continuously measuring the rate of corrosion of carbon steel in kraft liquors.

In the linear polarization method, the potential that is normally developed at the steel/liquor interface is raised or lowered by passing a controlled current through the steel and into the liquor. Based on electrochemical theory, the corrosion rate at any point in time is proportional to the current required to achieve the chosen shift in potential. Commercial instrumentation is available which will automatically perform these measurements and provide an estimate of the instantaneous rate of corrosion.

Although linear polarization methods have been used successfully in other industries, the unique chemistry of kraft white liquors raised some doubts about the accuracy of the method in these environments. There were concerns about interference in the electrical measurement by conductive deposits that form as a result of corrosion. A second concern was the possibility that chemical species present in the liquor could participate in the electrical reactions responsible for the current, thereby confusing the corrosion current measurements. The last area of

concern was the uncertainty over the magnitude of the constant of proportionality between the corrosion rate and the applied current determined in the measurement.

To resolve these concerns, tests were conducted to compare the average rate of corrosion measured by the linear polarization method and the actual rate of corrosion determined by weight loss measurement. A commercially available instrument was used to make the linear polarization measurements on plain carbon steel exposed to various simulated liquors.

The comparisons showed that the linear polarization method was generally a good indicator of corrosion rates in white liquors, but some modifications were required to make the method accurate. First, the constant of proportionality between the corrosion rate and the applied current that is inherent in the instrument was found to be in error, but this error could be eliminated by dividing the apparent corrosion rate by a factor of 2.3 to determine the actual corrosion rate.* Second, it was learned that liquor oxidation did occur on the carbon steel, but this only happened at a significant rate when the carbon steel spontaneously formed a protective film on its surface. Liquor oxidation, and the accompanying confusion in the linear polarization measurements only occurred when polysulfides (Na_2S_2) were present in the white liquor in large amounts, which also raised the potential at the metal/liquor interface to approximately 100 mV vs. the silver/silver sulfide reference potential. When there is doubt about errors in the linear polarization results due to liquor oxidation, a simple measurement of the metal potential will indicate whether these errors will be significant.

*Different correction factors will be appropriate for different commercial instruments, but these can be calculated easily based on the inherent constant for each instrument.

A few tests conducted in vigorously recirculated liquors revealed differences in the corrosion behavior compared to the usual test results for stagnant liquors. The corrosion rates in recirculated liquors were higher, and the correction factor needed to bring the linear polarization results into agreement with weight loss results differed from the 2.3 value appropriate for stagnant liquors. The effect of velocity on linear polarization results will be examined later in more detail; meanwhile, the correction factor of 2.3 should not be used in high flow situations.

The effect of various liquor constituents on the corrosion rate of carbon steel was examined as a part of this study. Thiosulfates and low concentrations of polysulfides accelerated the corrosion of carbon steel, whereas the concentration of sodium hydroxide and sodium sulfide had a lesser impact on the corrosion rate. Additions of sulfur in amounts greater than 2.5 g/L (to form Na_2S_2 in equivalent amounts) resulted in the passivation of carbon steel, with formation of a protective layer on the metal surface and a virtual cessation of corrosion.

Thus, the linear polarization method appears to be suitable for use in monitoring corrosion rates of carbon steel in white liquors, provided care is taken to calibrate the instrument and to avoid artifacts caused by reactions in the liquors. Several different types of commercial instrumentation can be used to monitor the corrosivity of white liquor, but the use of an instrument that simultaneously measures the voltage at the electrode — the "three-electrode instrument — is preferred because of the importance of potential measurements in detecting errors due to oxidation of liquor species. Instruments not provided by Petrolite may need different correction factors, but the appropriate correction factors can be determined empirically by (1) comparison of actual and measured weight loss, or (2) calculation

of a new factor as discussed in Appendix I. For the latter calculation, the vendor of the linear polarization instrument can provide the constants needed. Accurate measurement of the instantaneous corrosion rate by linear polarization should now be practical in pulp mill liquor, without the need for extensive training in corrosion engineering or electrochemistry.

INTRODUCTION

Corrosion of carbon steel equipment exposed to white liquor is a costly problem for the kraft pulping industry. Clarifiers, storage tanks, piping, and fittings suffer severe general corrosion that necessitates frequent replacement at considerable expense. Costs of maintenance and repair to these recausticizing components could be reduced if periods of high corrosion damage could be detected in time to take appropriate corrective measures.

One of the obstacles to a corrosion control strategy in white liquor systems is an inability to detect periods of high corrosivity in these liquors. Wensley (1) has reported that the corrosion rate measured in white liquor clarifiers could vary by an order of magnitude over a period of a few weeks (see Fig. 1). At the lowest rate of corrosion measured, most carbon steel equipment would last for the lifetime of the pulp mill; at the highest rate measured, most steel components would require replacement after a few years of operation. If it was possible to detect periods of high corrosion, mill personnel could take measures to reduce the corrosion rate and extend the life of the equipment.

It is known that changes in the concentration of minor constituents in kraft white liquor can have profound effects on the corrosivity of the liquor, although the exact mechanisms are not clearly understood. Polysulfides and thiosulfates, which are usually present at levels of less than 1% in white liquors, can cause a significant increase in white liquor corrosivity. Periods of high corrosivity in mill liquors are probably caused by inadvertent increases in the concentration of these compounds, perhaps as a result of changes in reduction efficiency at the recovery boiler. Since mills can operate successfully with liquors

producing low corrosion rates, corrective measures involving liquor control could be implemented to alleviate periods of high corrosion damage without affecting pulp mill operations.

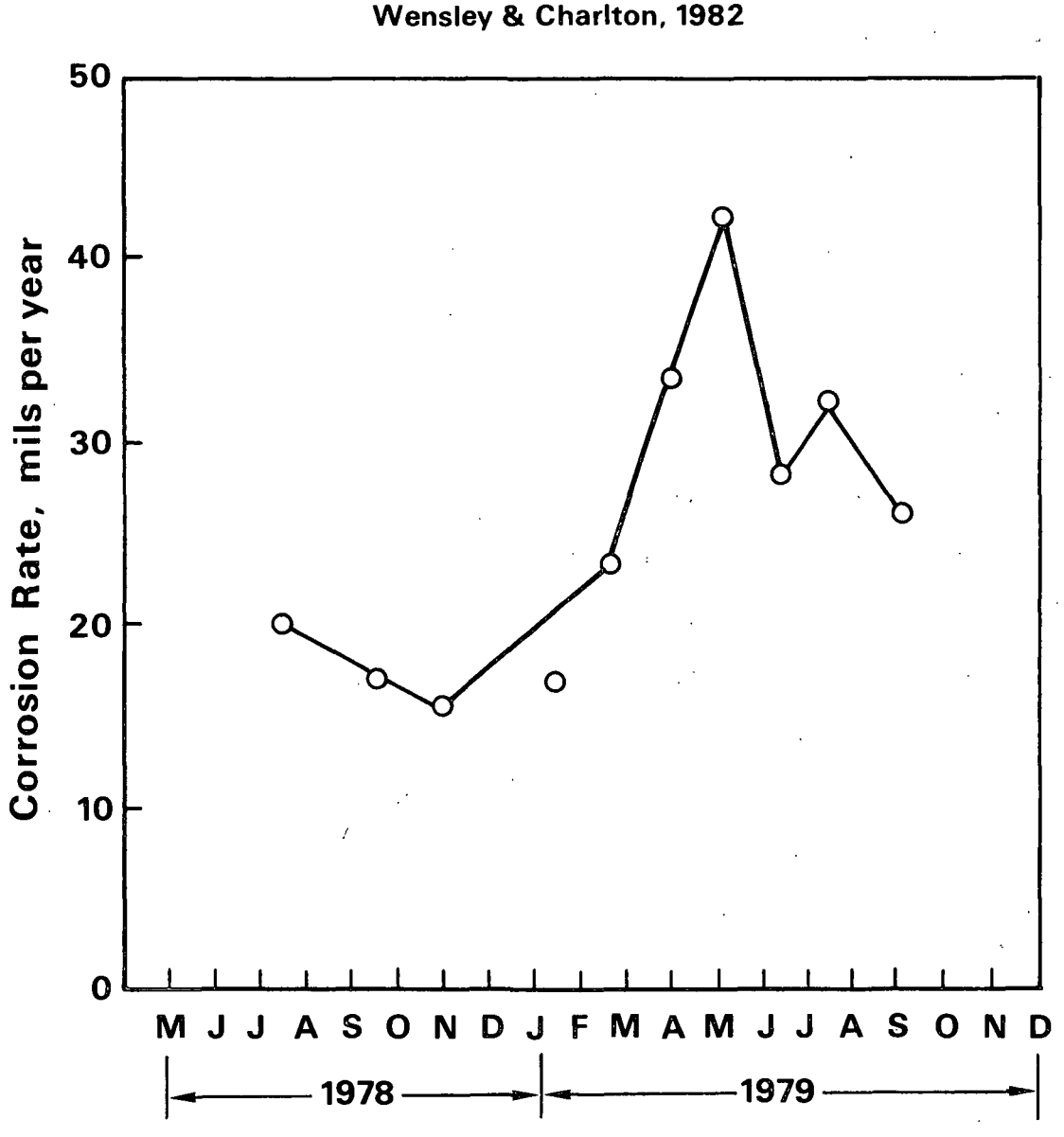

Figure 1. Variation in corrosion rate in a typical white liquor clarifier [Wensley and Charlton (1)].

To be effective, this corrosion control strategy requires the timely detection of periods of unacceptable corrosion damage. Weight loss coupons exposed to

the liquors could be used, but the use of such coupons is tedious and fails to provide timely information because exposure times are lengthy. The liquor species responsible for high corrosivity of white liquors could be determined by periodic chemical analysis, but the methods for such analysis are complicated and expensive, and do not provide for an instantaneous assessment of corrosion rate. On-line electrochemical methods are used to monitor corrosion rates in other industries, but these methods have not enjoyed widespread use in the pulp and paper industry.

One electrochemical method for instantaneous measurement of corrosion rates is the linear polarization (LP) method (2-3). In this method, an electrode immersed in the corrodant is subjected to an incremental voltage step by passing a controlled current through the metal/electrolyte interface and through another electrode (called the counter electrode) immersed in the electrolyte. Usually, the electrical potential developed at the metal/electrolyte interface is displaced only 10 mV or so by a device called a potentiostat —— a programmable, constant voltage power supply. The change in voltage at the test electrode is monitored with a voltmeter and a reference electrode immersed in the liquor. The reference electrode provides a stable benchmark or reference point against which other voltages can be measured. The current required to achieve a desired potential change is measured with an ammeter, as shown in Fig. 2. In the usual configuration, the reference electrode, test electrode, and counter electrode are all inserted into the electrolyte on a probe as shown in Fig. 3.

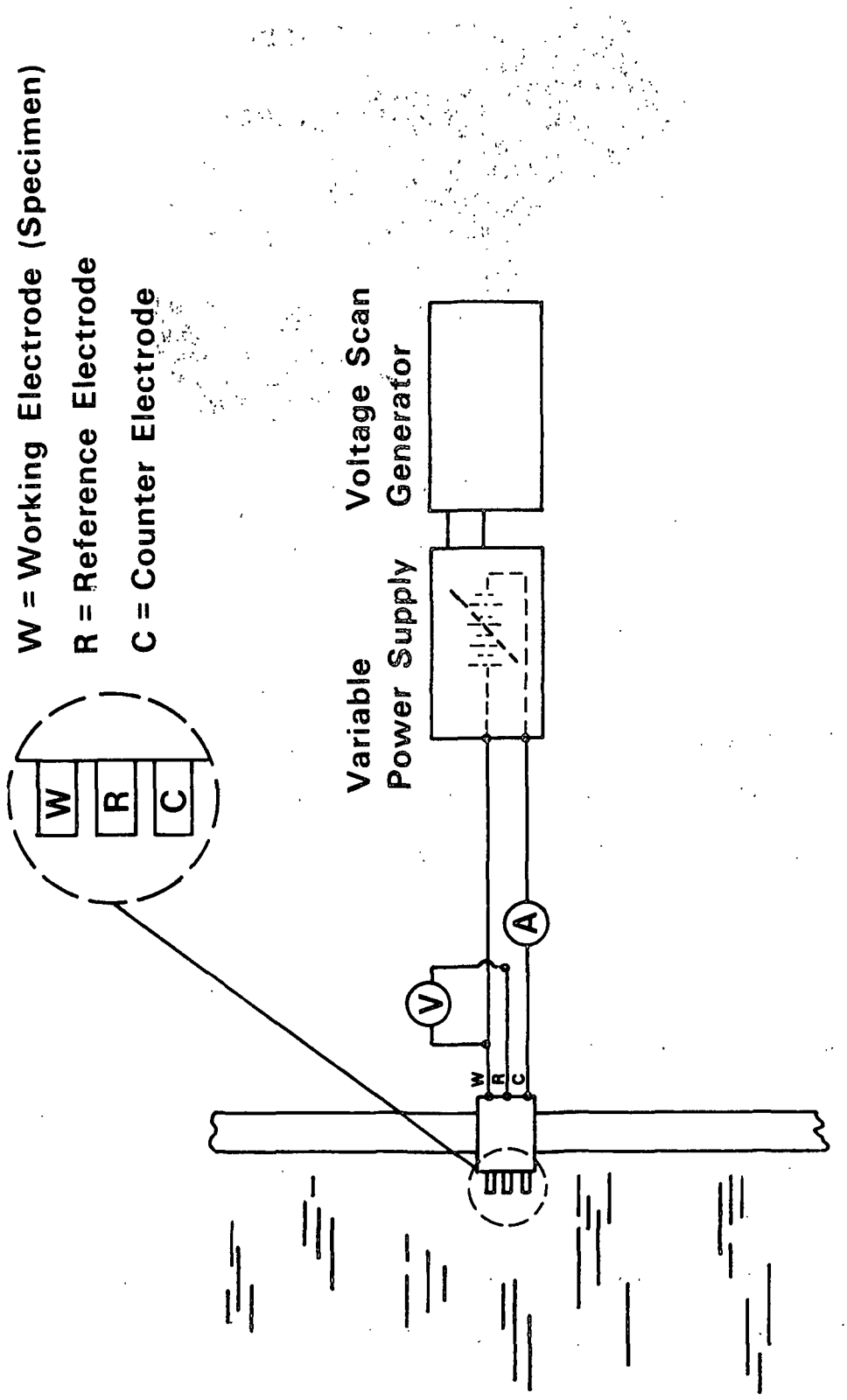

Figure 2. Schematic diagram of the apparatus required for linear polarization measurements.

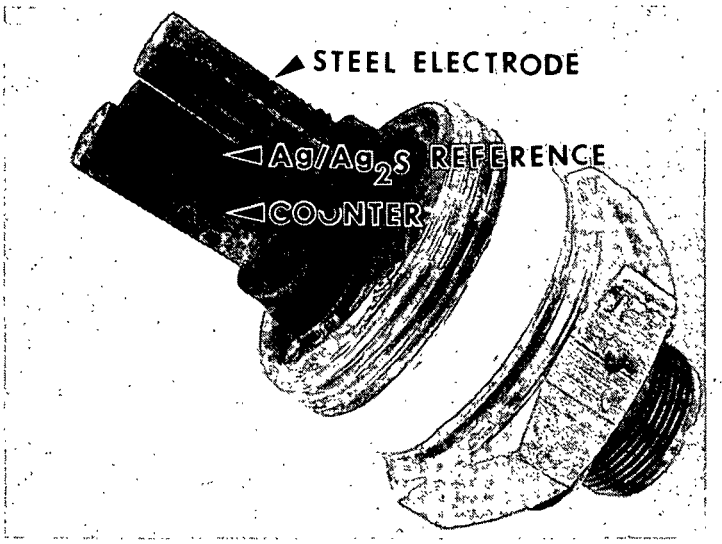

Figure 3. A typical sensor probe used in linear polarization studies, with a mounted working electrode, reference electrode, and counter electrode.

The corrosion rate of the working electrode is determined by the current required to shift the potential (i.e., to polarize) the electrode by a fixed amount —— usually 10 mV. If several assumptions are made regarding the mechanism of corrosion, the ratio of applied current to applied voltage is proportional to the corrosion rate. The corrosion rate is given by the equation

$$CR = \left(\frac{1}{2.3F}\right)\left(\frac{\Delta i}{\Delta E}\right)(\beta/Z)\left(\frac{MW}{D}\right) \qquad (1)$$

where F is Faraday's Constant (F ≅ 96,500 coulombs/mole of electrons), $\Delta i/\Delta E$ is the ratio of induced current to applied voltage, β is a constant determined by the electrochemical characteristics of the metal in the liquor, Z is the number of electrons released when a metal atom is dissolved, and MW and D are the molecular weight and density of the dissolving metal, respectively. For dissolution of steel, MW = 55.8 grams/mole and D = 7.87 grams/cm^3. If the dissolution reaction is

$$Fe \longrightarrow Fe^{++} + 2e^{-} \qquad (2)$$

Z will have a value of 2 electrons/atom. The β constant is a characteristic of two constants, β_a and β_c, which describe the anodic and cathodic reactions occurring during corrosion. β is given by

$$\beta = \frac{\beta_a \beta_c}{\beta_a + \beta_c} \qquad (3)$$

and β, β_a, and β_c have units of mV. A detailed discussion of β is beyond the scope of this report, but some discussion is provided in Appendix I and Mansfeld (3) discusses the origins of the β term in depth.

If $\Delta i / \Delta E$ is measured on an electrode immersed in an electrolyte, the corrosion rate of the electrode can be calculated via Eq. (1), with some assumptions about the values of the constants, β and Z. If the test electrode is made of the same material as the wall of a vessel, for example, the corrosion rate of the wall can be estimated by utilizing the linear polarization method on a probe inserted near the vessel wall. Under ideal circumstances, β_a, β_c, and Z can be determined independently of the linear polarization equation and Eq. (1) can be applied directly. In less ideal circumstances, the value of β/Z must be established empirically by simultaneous weight loss and linear polarization measurement for subsequent use in Eq. (1). Commercial instrumentation and probes are available* for linear polarization measurements in process liquor streams.

Instantaneous corrosion rate measurements based on linear polarization may not be reliable in white liquors for a variety of reasons discussed in general terms by Mansfeld (3). For example, many of the sulfur-bearing species present in white

*Two vendors of linear polarization instrumentation for corrosion rate measurement are Petrolite Instruments, Houston, TX and Rohrback Instruments, Santa Fe Springs, CA.

liquors are able to participate in electrochemical reactions that may masquerade as dissolution of carbon steel. Reactions such as

$$2S^{=} \longrightarrow S_2^{=} + 2e^{-} \qquad (4)$$

and

$$S_2O_3^{=} + 3H_2O \longrightarrow 2SO_3^{=} + 6H^{+} + 4e^{-} \qquad (5)$$

can occur on the carbon steel substrate, and the electrons released would be indistinguishable from electrons produced by

$$Fe \longrightarrow Fe^{++} + 2e^{-} \; . \qquad (2)$$

The linear polarization method utilizes the total induced current accompanying a voltage change —— including both metal oxidation and liquor oxidation —— and may result in excessively high estimates of corrosion rates if species in the liquors can react to liberate electrons.

A second possible source of error in linear polarization measurements arises from the thick, sulfide-rich film that forms when carbon steel is exposed to white liquors. These films may be conductive because they contain a preponderance of conductive sulfide species such as FeS. The films could interfere with measurement of the polarization resistance, $\Delta E/\Delta i$, or they could short-circuit the sensing electrodes by forming a contiguous, conductive deposit.

A third potential source of error in linear polarization measurements in white liquor is the uncertainty regarding the Tafel slope constant, β, and the oxidation number, Z, in the corrosion rate equation, Eq. (1). The appropriate values of β_a and β_c required to calculate β by Eq. (3) are difficult to establish independently because film formation restricts the extent of Tafelian behavior needed to

determine the Tafel slopes (see Appendix I for details). Moreover, the number of electrons liberated when one iron atom dissolves at the surface of carbon steel is uncertain. The value of Z is likely to be 2, corresponding to Eq. (2) or

$$Fe + 2H_2O \longrightarrow HFeO_2^- + 3H^+ + 2e^- \qquad (6)$$

but further oxidation of iron may proceed in part by a reaction such as

$$Na^+ + 2S^= + Fe^{++} \longrightarrow NaFeS_2 \downarrow + e^- \qquad (7)$$

which would raise the net oxidation number to 3. The two uncertain quantities, β and Z, appear in the corrosion rate equation as a ratio, (β/Z).

The objective of this ongoing study is to qualify the linear polarization method for use by the pulping industry to monitor corrosion rates in kraft white liquor. Linear polarization studies have been conducted in the laboratory to evaluate the feasibility of using the LP method for corrosion rate measurements on carbon steel exposed to actual white liquors. Weight loss coupons were exposed to white liquors while linear polarization measurements were being made in the same liquors. The accuracy of the linear polarization test was examined by comparing the LP weight loss (determined by time-integration of the corrosion rate measured by linear polarization) and the actual weight loss caused by corrosion of the coupons. Supplementary tests were conducted to establish the electrochemical characteristics of carbon steel in the white liquors. Attempts were also made to determine appropriate values of β and Z from independent measurements.

EXPERIMENTAL PROCEDURES

Linear polarization measurements were made using two types of instrumentation. A commercial, 10 channel Petrolite Model 1010 was used for most of the corrosion rate determinations, with occasional use of a Princeton Applied Research Model 350 Corrosion Instrument. The Petrolite instrument was programmed to impose alternate +10 mV and -10 mV polarizations of 15 minutes duration on each of eight electrodes. The open circuit potential, E_{corr}, developed at the electrodes was also determined prior to the 10 mV polarizations.

Currents required to maintain the 10 mV polarizations were captured by the instrument at the end of the 15-minute cycle and converted into an output signal proportional to the corrosion rate in mils/year (mpy). The instrument is hard-wired with a (β/Z) value of 41.65 mV for carbon steel electrodes with a specified surface area of 9 cm^2. Alternative values of (β/Z) can be accommodated by multiplying the mpy output reading of the instrument by an appropriate calibration constant.

The output data for each successive LP measurement were acquired using an Apple IIe microcomputer with an ISSAC 91A interface unit. Data were acquired, stored, plotted, and printed automatically. The corrosion rate for each specimen was integrated as a function of time using a Simpson's Rule routine to calculate the average weight loss corresponding to the linear polarization measurements. In general, both LP results and weight loss results are presented as an average corrosion rate over the period of exposure.

Weight loss data were obtained from multiple coupons exposed to the liquors at the same location and for the same period of time as the electrodes used in the LP measurement. Both weight loss coupons and LP electrodes were cylinders with a

surface area of 9 cm^2. Heavy black films found on the weight loss coupons following exposure were removed by brief immersion in an inhibited Clarke's solution (4); in some cases, adherent deposits were removed by mild abrasion followed by acid cleaning in Clarke's solution.

The specimens tested in this program were manufactured from a 1018 carbon steel with the composition shown in Table I. The steel was provided in the form of hot rolled bar stock, 3/8-inch O.D., which was turned, tapped, and ground to a 120 grit finish before testing.

TABLE I

COMPOSITION OF AISI 1018 CARBON STEEL

Carbon	0.16% by weight
Manganese	0.68%
Silicon	0.06%
Phosphorous	0.008%
Sulfur	0.024%
Iron	Balance

Coupons and electrodes were exposed simultaneously to test solutions at 90°C in two types of Teflon® chambers. For most of the tests, the coupons and electrodes were exposed in 100 mL Teflon jars installed in a heated water bath; the solutions in these chambers were stagnant. Threaded rods fastened to the specimens penetrated the lid of the Teflon jar to provide access for LP measurements and rest potential measurements. The reference electrode used in these tests was a directly immersed silver/silver sulfide electrode as described in a previous report (5). The counter electrode was a graphite rod. The chambers used for these tests are shown in

®Du Pont Corp.

Fig. 4. In a few cases, coupons and electrodes were exposed in larger chambers where the solutions were vigorously recirculated to increase the corrosion rate and vary the conditions for evaluation of the LP method. In all cases except those involving deliberate aeration, the solutions were prepared and maintained under a prepurified nitrogen cover gas to prevent oxidation of liquor species during testing.

In addition to the simultaneous LP and weight loss measurements, several tests were conducted using weight loss coupons (without simultaneous LP measurements) to establish corrosion characteristics over a wider range of conditions. Coupons were exposed for two, four, six, and eight weeks with weight loss measurements made after each two-week exposure. The rest potentials of these specimens were also measured daily throughout the exposure to map changes in E_{corr} with time. These exposures were made in stagnant liquors containing NaOH and Na_2S in the range 0-140 g/L and 0-45 g/L, respectively.

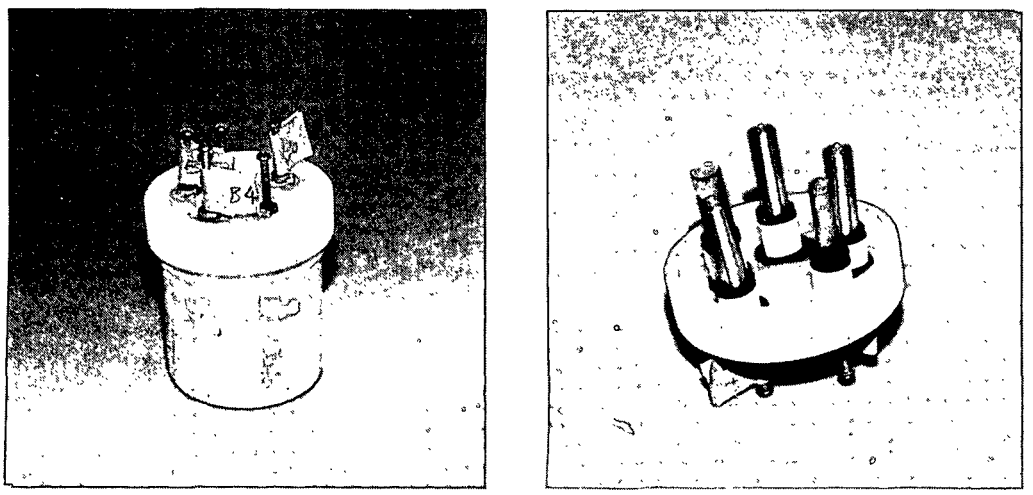

Figure 4. Test chambers used in studies of corrosion in stagnant liquors.

RESULTS

CORROSION WEIGHT LOSS MEASUREMENTS

The corrosion behavior of carbon steel exposed to alkaline sulfide environments was rich in variety. The average corrosion rates measured on coupons removed after various exposures in $NaOH/Na_2S$ solutions are listed in Table II.

TABLE II

AVERAGE CORROSION RATES+ FOR CARBON STEEL EXPOSED TO SIMULATED WHITE LIQUORS (mils/year)

Time, weeks	NaOH, g/L	Na_2S, g/L ——> 0	10	15	20	25	30	35	40
2	0		0.2			0.8			0.7
4	0		0.2			0.9			0.7
6	0		0.0			0.9			0.4
8	0		*			0.5			0.9
2	60	*,*	2.5	2.9	3.1	4.3	0.0	2.5	5.4
4	60	*,*	0.9	1.5	1.4	1.3	0.3	0.7	2.1
6	60	*,0.3	0.6	1.2	1.3	0.7	0.1	0.6	2.7
8	60	*	0.5	1.2	0.9	0.6	0.1	0.5	3.4
2	80	0.1,0.0	3.0			3.6			5.3
4	80	0.0,0.0	1.2			3.2			0.6?
6	80	0.0,0.0	0.8			3.9			4.8
8	80	*	0.6			3.6			4.9
2	100	*,*	3.2	3.8	3.6	3.6	3.8	3.3	3.7
4	100	0.1,*	3.1	3.3	3.6	3.2	3.4	3.0	3.1
6	100	0.0,1.2	3.1	2.5	2.6	3.5	4.2	4.0	4.1
8	100	0.1	1.7	2.2	2.6	3.8	3.6	4.4	5.2
2	120	4.0	3.4			7.1			7.3
4	120	1.2	3.4			5.5			6.2
6	120	2.0	2.8			4.6			4.6
8	120								
2	140	0.6	5.9	7.5	6.9	7.4	6.7	5.9	5.4
4	140	3.0	4.8	4.8	4.7	5.2	5.4	4.5	4.2
6	140	5.8	3.9	3.9	3.8	4.4	4.0	3.6	3.7
8	140								

* = Weight gain.
+ = Determined by weight loss measurement.

Corrosion of carbon steel in pure NaOH solutions at 90°C was relatively uncomplicated. If the concentration of NaOH was below 100 g/L, the carbon steel was not susceptible to significant corrosive attack. Some of the coupons exposed to caustic solutions at low concentrations showed a slight weight increase as the result of formation of a protective film. For sodium hydroxide concentrations above 100 g/L, a corrosion rate of approximately 3 mpy was observed. There was some evidence of an incubation period preceding the onset of corrosion in the solutions containing 140 g/L NaOH.

For most of the exposures of carbon steel to pure NaOH solutions, the open circuit potential of the steel became more noble as the time of exposure increased. Typically, the potential developed at the metal/liquor interface would first be in the range, -600 to -400 mV vs. the saturated Calomel electrode (SCE) potential. After approximately 50 hours of exposure to pure NaOH solutions, the open circuit potential had risen to a rest potential in the vicinity of -350 mV SCE, where it remained for the balance of the test. Generally speaking, the eventual rest potential of carbon steel was slightly more negative for more concentrated caustic solutions. Plots of the open circuit potential as a function of time are shown in Fig. 5 for tests in several caustic solutions. In a few cases, the corrosion potential fluctuated by approximately 100 mV during the exposure, but these fluctuations had no discernible effect on the observed weight loss. The weight loss measurements and the increases in rest potential are characteristic of corrosion inhibition by formation of a protective film on the surface of the carbon steel, as reported by several other investigators (6,7).

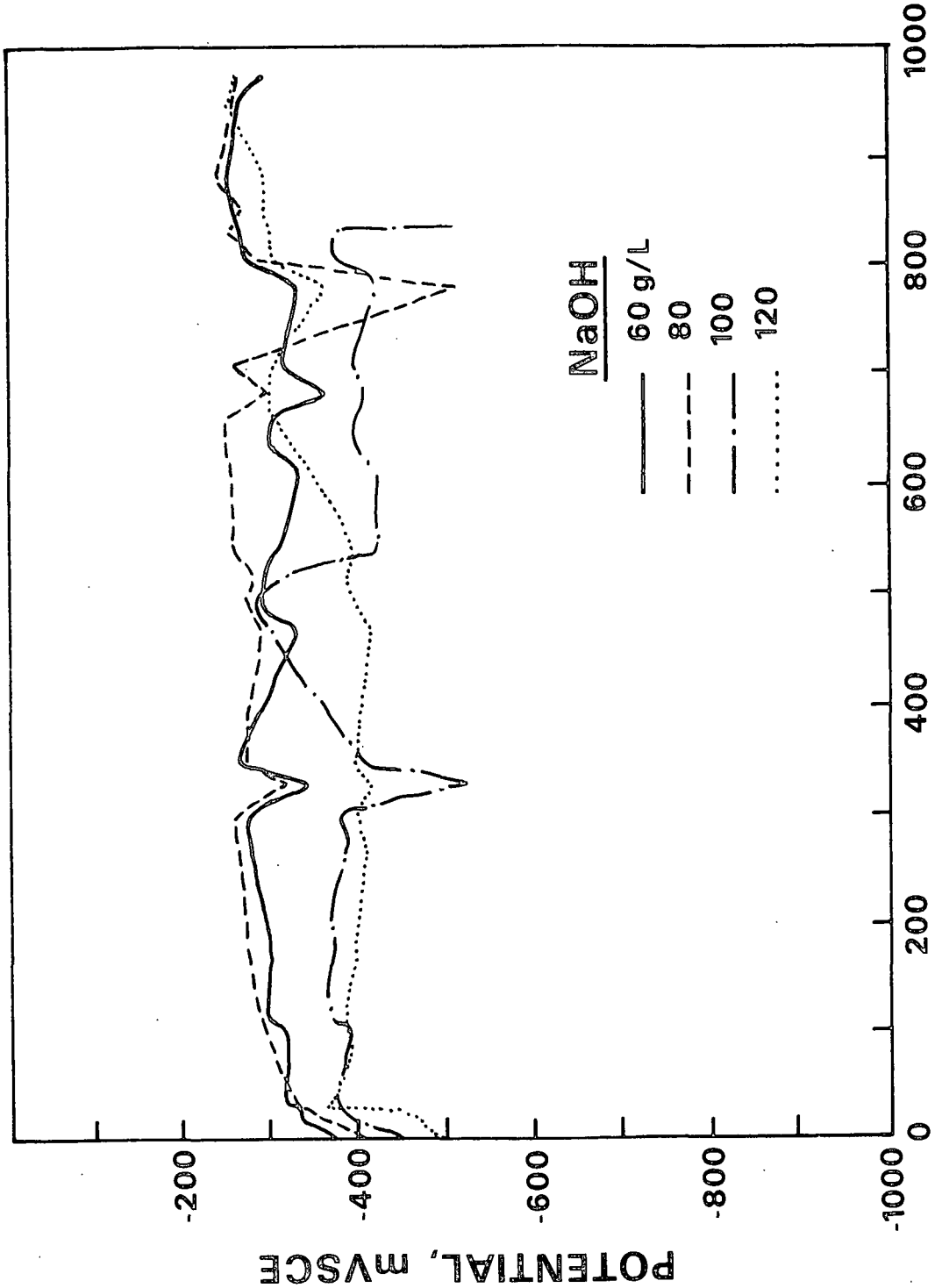

Figure 5. Potential vs. time for carbon steel exposed to several pure caustic solutions, showing passive behavior.

Similarly, carbon steel exposed to solutions containing only sodium sulfide additions also exhibited very low rates of corrosion —— less than 1 mpy in all cases. The corrosion rates remained low in spite of the development of considerable alkalinity as a result of sodium sulfide hydrolysis reactions. As in the case of the tests in pure NaOH solutions, the potential of the carbon steel in pure Na_2S solutions increased in the noble direction as the time of exposure increased. The final rest potential ultimately achieved depended on the concentration of sodium sulfide in the solution. In solutions containing 10 g/L Na_2S, the rest potential was between +100 mV vs. silver/silver-sulfide (-775 mV SCE) and +150 mV SSS (-825 mV SCE). In solutions containing 25 or 40 g/L Na_2S, the rest potential of carbon steel was in the range, -100 to -50 mV SSS (-1000 to -950 mV SCE). In two cases, carbon steel electrodes exposed to 40 g/L Na_2S exhibited potentials that first rose to +100 mV SSS and then dropped to -100 mV SSS for the balance of the exposure. The low corrosion rates and noble shifts in rest potential observed in solutions containing only Na_2S is suggestive of protection resulting from the formation of a protective film.

The corrosion behavior in solutions containing moderate levels of both caustic and sulfide was more complicated, reflecting a change from active to passive behavior during the exposures.

In solutions containing a moderate amount of NaOH and Na_2S, the corrosion rate during the first two-week exposure was 2 to 5 mpy, but fell to lower levels thereafter (Table II). Coupons exposed for four, six, and eight weeks exhibited the same weight loss as coupons exposed for only two weeks. This behavior was observed in simulated liquors containing 60 g/L NaOH and 10 to 30 g/L Na_2S, or 80 g/L NaOH and 10 g/L Na_2S.

Solutions containing higher levels of caustic and sulfide produced a constant level of corrosion throughout the eight-week exposures, with no evidence of cessation of corrosion after prolonged exposure. The corrosion rate was more or less uniform at 3 to 5 mpy for solutions containing 60 g/L NaOH and 40 g/L Na_2S, 80 g/L NaOH and 25 to 40 g/L Na_2S, or more than 100 g/L NaOH. Anomalous behavior was observed in the solution containing 60 g/L NaOH and 30 g/L Na_2S; carbon steel remained uncorroded throughout the entire eight-week exposure in this solution.

The potentials measured during the eight-week exposure confirmed the apparent transition from active corrosion (at 5 mpy) to passivation (at less than 1 mpy) observed in the weight loss studies. When a steel specimen was actively corroding at a rate of 5 mpy or so, the potential developed at the metal/liquor interface was about 240 mV below the SSS reference potential. Those specimens that were immune from corrosion in alkaline sulfide liquors usually exhibited a rest potential approximately 100 mV above the SSS reference potential, corresponding to approximately -800 mV SCE. In solutions where the corrosion behavior was initially active followed by passivation, the potential measured at the metal/liquor interface was initially at -240 mV SSS but gradually increased to +100 mV SSS as the protective film was established. Once the potential reached the +100 mV SSS level, corrosion virtually ceased. In a few cases, an intermediate potential of -100 mV SSS was established at the metal/liquor interface. Usually, this was associated with a low average rate of corrosion (~ 1 mpy), perhaps as the result of incomplete or imperfect formation of the protective film. Examples of changes in corrosion potential for three different types of corrosion behavior —— active, passive, and active-passive —— are shown in Fig. 6. The anomalous passivation of steel exposed to the liquor containing 60 g/L NaOH and 30 g/L Na_2S described above was accompanied by an early transition to the +100 mV SSS potential.

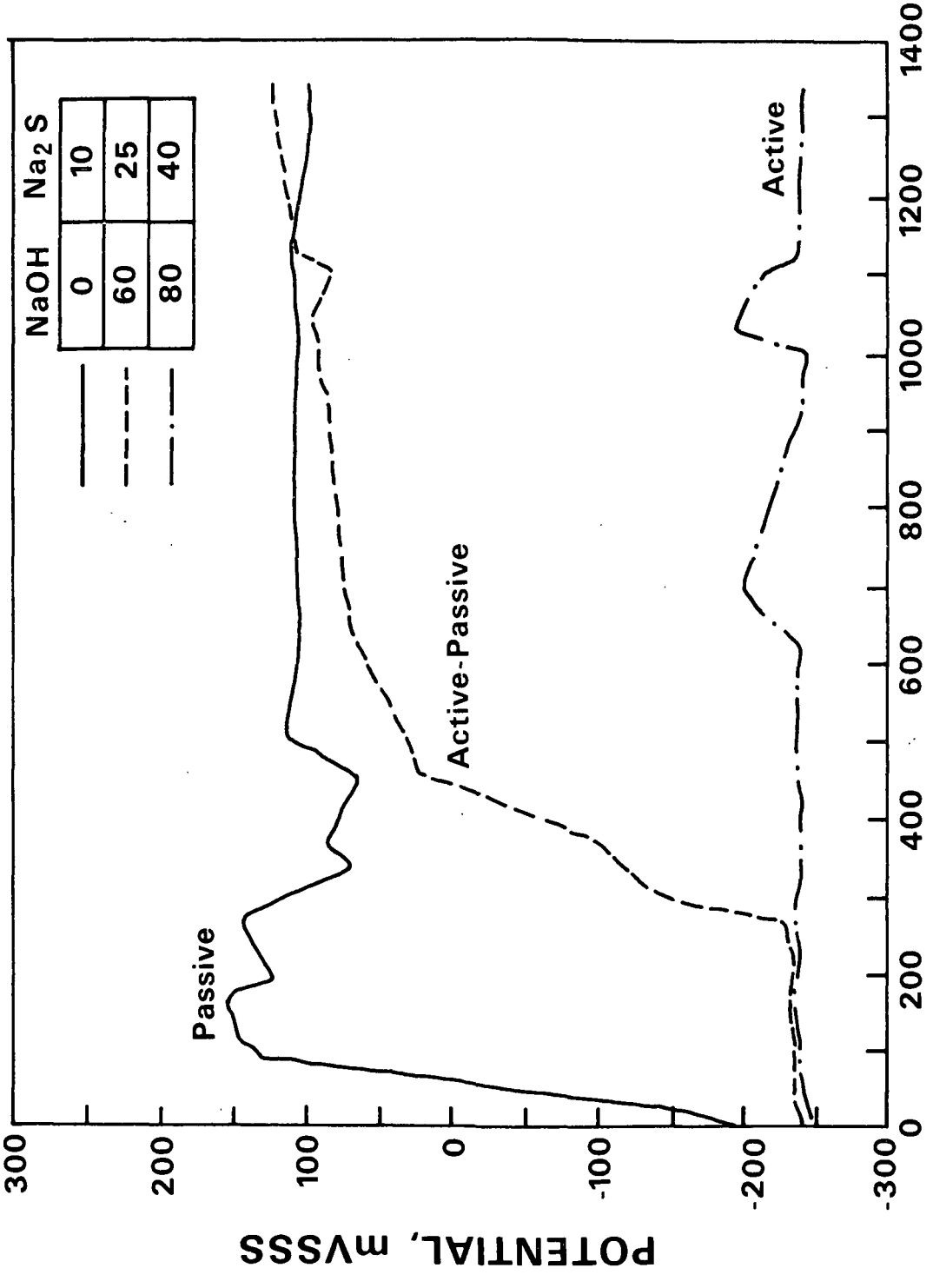

Figure 6. Potential changes as a function of exposure time for typical active, passive, and active-passive conditions.

In some cases, the transition from active corrosion to passivation occurred when the test chamber was opened to retrieve a weight loss coupon after an initial exposure. This transfer was accomplished in a nitrogen-filled glove bag, so the transition was probably not caused by oxygen effects on the film or the solution. The active-to-passive transition may have been triggered by the momentary loss of temperature or the agitation associated with the specimen removal.

The three rest potentials exhibited by carbon steel in alkaline sulfide media coincide with observable changes in the electrochemistry of iron in these alkaline sulfide solutions. The -240 mV SSS potential associated with active corrosion coincides with the onset of a second cathodic process that is probably the hydrogen reduction reaction. Two cathodic processes occurring on an inert gold electrode during cathodic polarization are shown in Fig. 7. The first cathodic reaction occurring on the noble metal electrode is probably associated with reduction of either dissolved oxygen at trace levels or —— more likely —— with reduction of polysulfide. This first reduction process is not quite capable of supporting a corrosion rate corresponding to 5 mpy on iron at the -240 mV SSS potential. A second reduction process becomes apparent at a potential of ~ -200 mV SSS, and it is this second cathodic process that can support a corrosion current equivalent to a 5 mpy corrosion rate on iron, as shown schematically in Fig. 8. The second reduction process is also observed in deaerated, pure NaOH solutions and is probably due to the reaction shown in Eq. (8).

$$2H_2O + 2e^- \longrightarrow 2OH^- + H_2, \qquad (8)$$

which has a standard half cell potential at pH = 14 of -170 mV SSS. Thus, the mixed potential of -240 mV SSS for active corrosion at a rate of ~ 5 mpy is fixed at the potential where the anodic current due to metal dissolution is equal to a cathodic current that is augmented by the hydrogen evolution reaction.

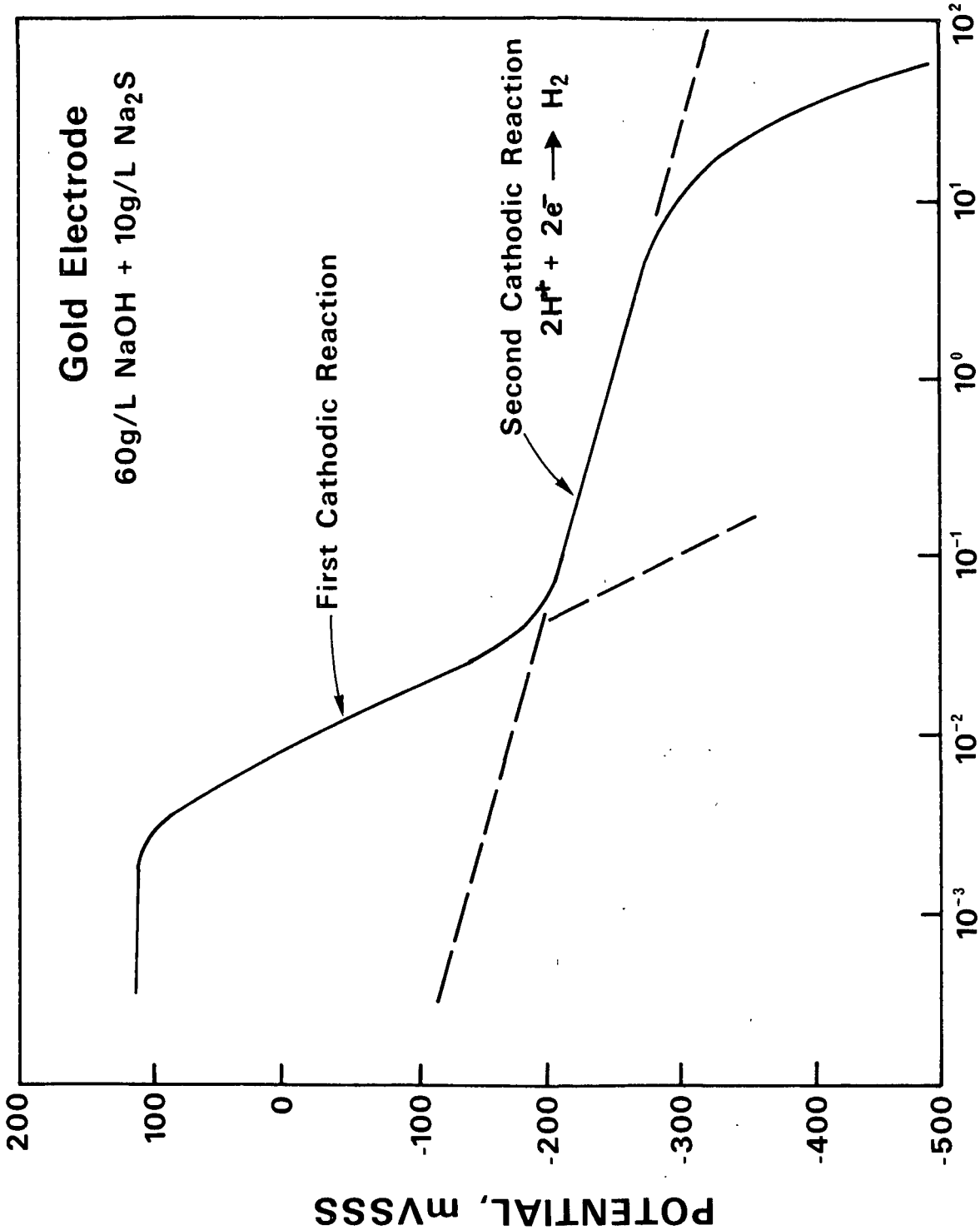

Figure 7. Cathodic polarization curve for gold in a 60 g/L NaOH, 10 g/L Na_2S solution, showing two successive reduction processes.

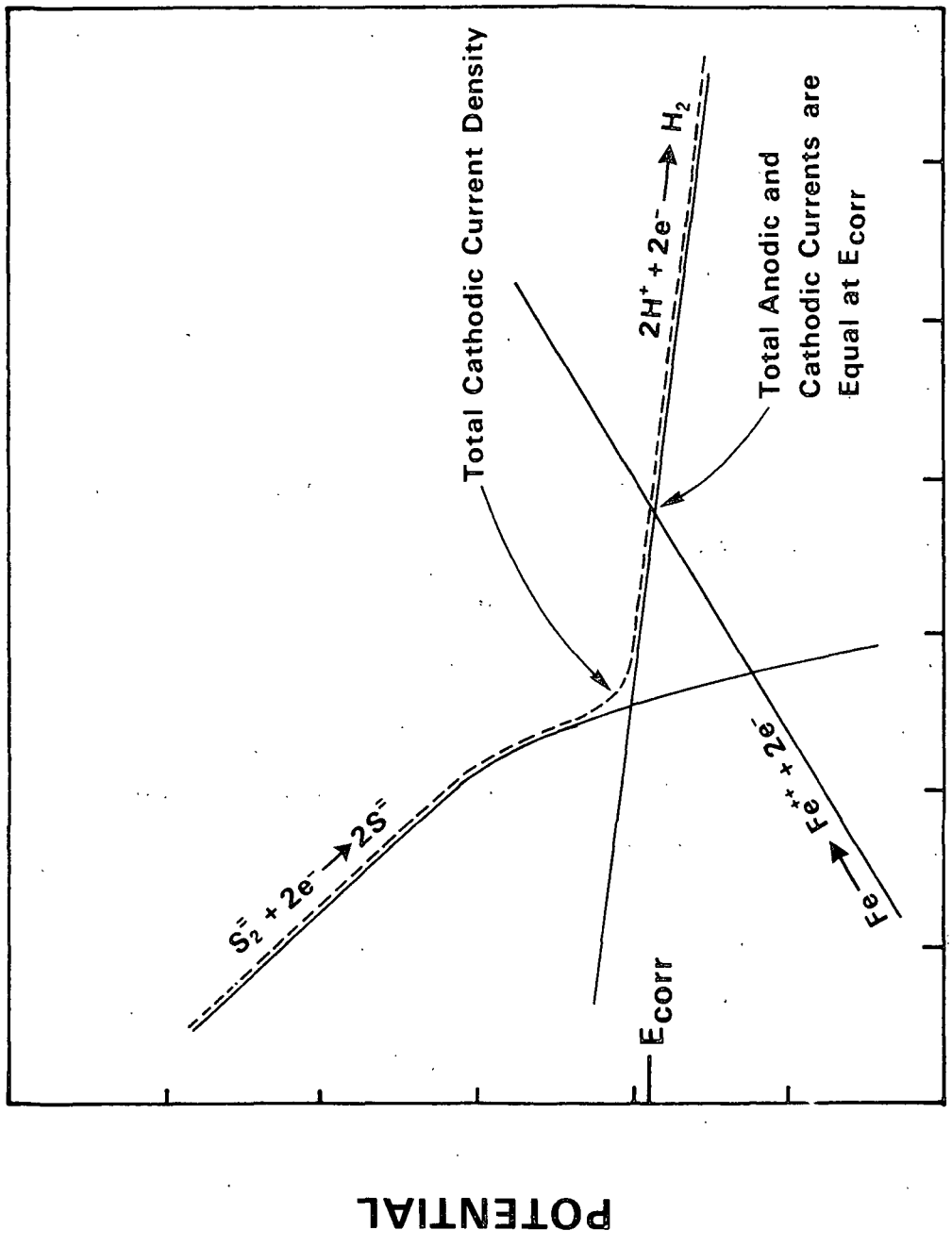

Figure 8. Schematic diagram showing the role of the hydrogen reduction reaction in establishing the rest potential of iron in alkaline sulfide solutions.

The +100 mV SSS potential associated with complete passivation of carbon steel coincides with the redox potential observed on gold and stainless steels in alkaline sulfide solutions. Apparently, the passivated carbon steel acts as an inert host for the same redox reactions that establish the redox potential on gold. These redox reactions may involve polysulfide in a reaction of the type

$$S^{=} + S_x^{=} \rightleftharpoons S_{x+1}^{=} + 2e^{-} \qquad (9)$$

Apparently, the current required to maintain the passive film is relatively small compared to the oxidation current derived from reaction (9), so the redox potentials of passivated carbon steel and gold coincide.

The intermediate potential of -100 mV SSS is apparently not a simple mixed potential involving active dissolution and a coupled cathodic process, since the corrosion rate is lower at this more noble potential. If the mixed potential was established by a balance between active dissolution and a complementary reduction process, the rate of dissolution at the more noble potential would be higher, rather than lower. Incomplete formation of a passive film on carbon steels could be responsible for this intermediate potential.

The reproducibility of the corrosion rate under active corrosion conditions was examined by exposing 24 weight loss couponds in eight separate chambers containing solutions with 100 g/L NaOH and 33 g/L Na_2S at 90°C. After a two-week exposure, the average corrosion rate in this environment was 3.4 mpy and the standard deviation was 1.3 mpy. These values agree well with the results shown in Table II.

Additional tests were conducted to examine the effects of minor constituents in the white liquors on corrosion rates of carbon steels. The effects of oxygen exposure, sodium thiosulfate and sulfur (forming sodium polysulfide, Na_2S_x) were

investigated by adding various amounts of those species to a reference liquor (100 g/L NaOH and 33 g/L Na_2S) and conducting weight loss studies in these modified electrolytes. Most of these tests were conducted in stagnant liquors, but a few were conducted in liquors that were vigorously recirculated to raise the corrosion rate.

Thiosulfate additions to these simulated liquors caused a marked increase in the corrosion rate of carbon steel, as predicted by Haeglund and Roald (8), Wensley and Charlton (9), and others. The corrosion rate increased as the concentration of $Na_2S_2O_3$ increased, reaching saturation at 25 g/L $Na_2S_2O_3$ as shown in Fig. 9. As little as 2.5 g/L $Na_2S_2O_3$ increased the corrosion rate by a factor of two relative to the corrosion rate observed in thiosulfate-free solutions (even though the corrosion rate in the reference liquor was high compared to previously cited rates). In solutions containing 25 g/L $Na_2S_2O_3$, which would represent an extraordinary dead load in an actual mill liquor, the corrosion rate was nearly four times as large as the corrosion rate in the thiosulfate-free reference liquor. The high rate of corrosion in thiosulfate-doped solutions was accompanied by formation of a greenish-black $NaFeS_2$ film on the surface of the specimen. Occasionally, this film spalled off the specimens in sheets and remained intact at the bottom of the test chamber. The rest potential of carbon steel exposed to solutions doped with 5 g/L or less of $Na_2S_2O_3$ remained at the usual -240 mV SSS level throughout the 18-day exposures. The rest potential of carbon steel in the solution doped with 25 g/L of $Na_2S_2O_3$ climbed to the -100 mV SSS level during the test.

Additions of small amounts of elemental sulfur to the reference solution containing 100 g/L NaOH and 33 g/L Na_2S increased the corrosion rate, whereas larger concentrations (> 2 g/L S^o) induced passivation and reduced the corrosion rates to

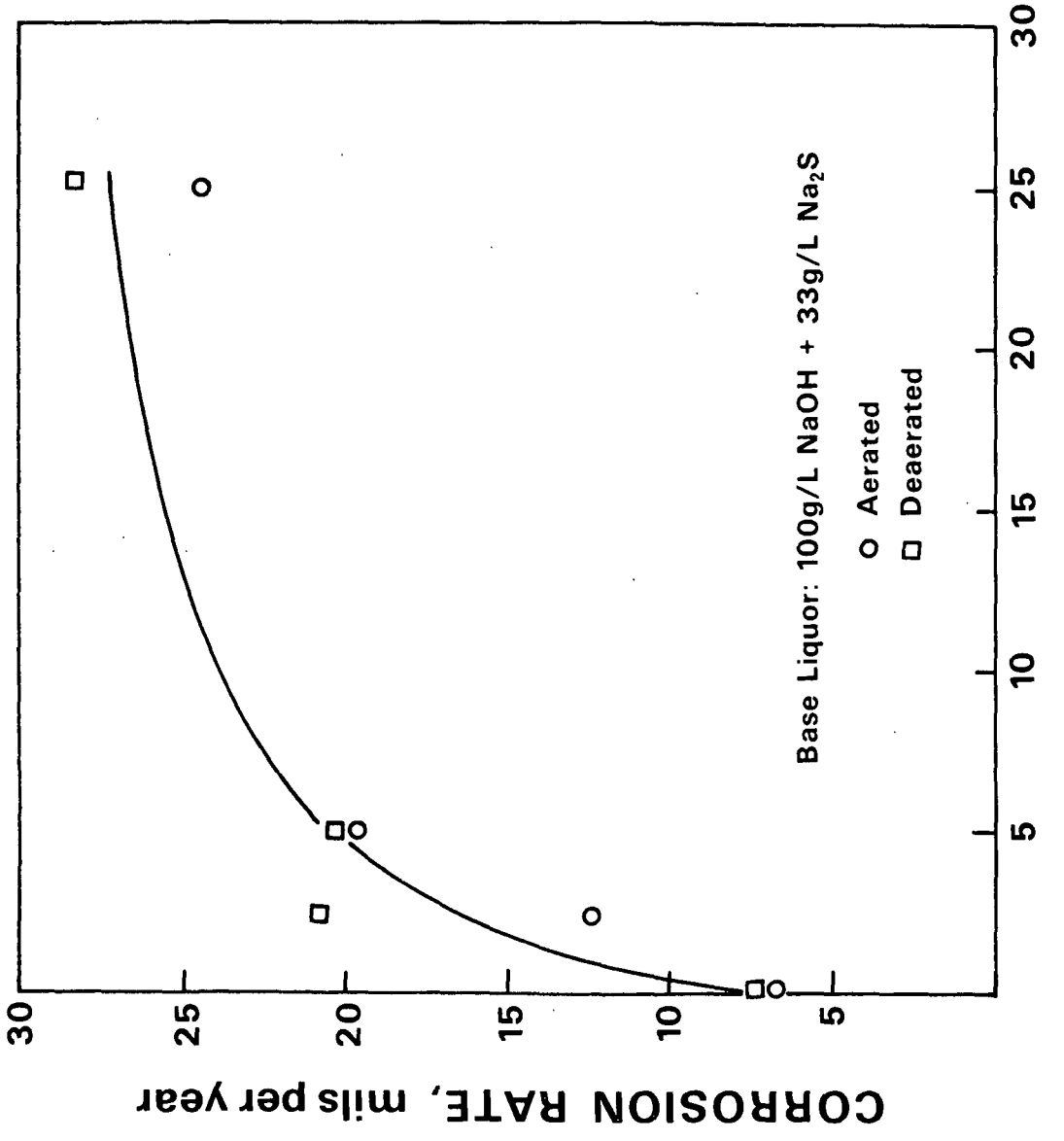

Figure 9. Effect of thiosulfate concentration on the rate of corrosion of carbon steel in a simulated white liquor containing 100 g/L NaOH and 33 g/L Na_2S.

insignificant levels. Similar results were reported by Hassler (10), Ahlers (11), Mueller (12), and others. In the present study, the corrosion rate in the presence of 0.5 g/L S^o increased by 50% over the rate observed in the absence of polysulfide, and the effect might have been larger if the polysulfide had not been consumed during the exposure. Additions of 2.5 g/L S^o to the reference liquor increased the corrosion rate by a factor of 2 to 3, but further increases in the polysulfide concentration curtailed active corrosion. At 5 to 10 g/L S^o, the corrosion rate fell to less than 3 mpy for five of six coupons; the exceptional coupon exposed to the 5 g/L S^o solution continued to corrode at the rate of 14 mpy. The average corrosion rates in the polysulfide solutions are shown in Fig. 10.

As would be expected with the addition of a polysulfide oxidant, the rest potential of the carbon steel coupons increased with increasing $S_x^=$ concentration. In solutions containing 0.5 g/L S^o, the carbon steel potential remained at -240 mV SSS, corresponding to active corrosion under the predominant influence of hydrogen reduction as the cathodic process. In solutions doped with 2.5 g/L S^o, the rest potential drifted in the range, -80 to -140 mV SSS, corresponding to a mixed potential established by the polysulfide reduction reaction. The addition of 5 or 10 g/L S^o promoted complete passivation at a rest potential in the range, 100 to 120 mV SSS.

Although waterline attack is frequently observed in white liquor vessels, dissolved oxygen had little effect on the corrosion rate of carbon steel exposed to simulated liquors. As shown in Fig. 9, the corrosion rates were virtually identical in thiosulfate doped solutions regardless of whether the solutions were aerated or deaerated. No attempt was made to characterize the extent of oxygen consumption by sulfoxy compound formation during these tests. Based on the results of Mueller (13), the consumption of dissolved oxygen could have been virtually complete.

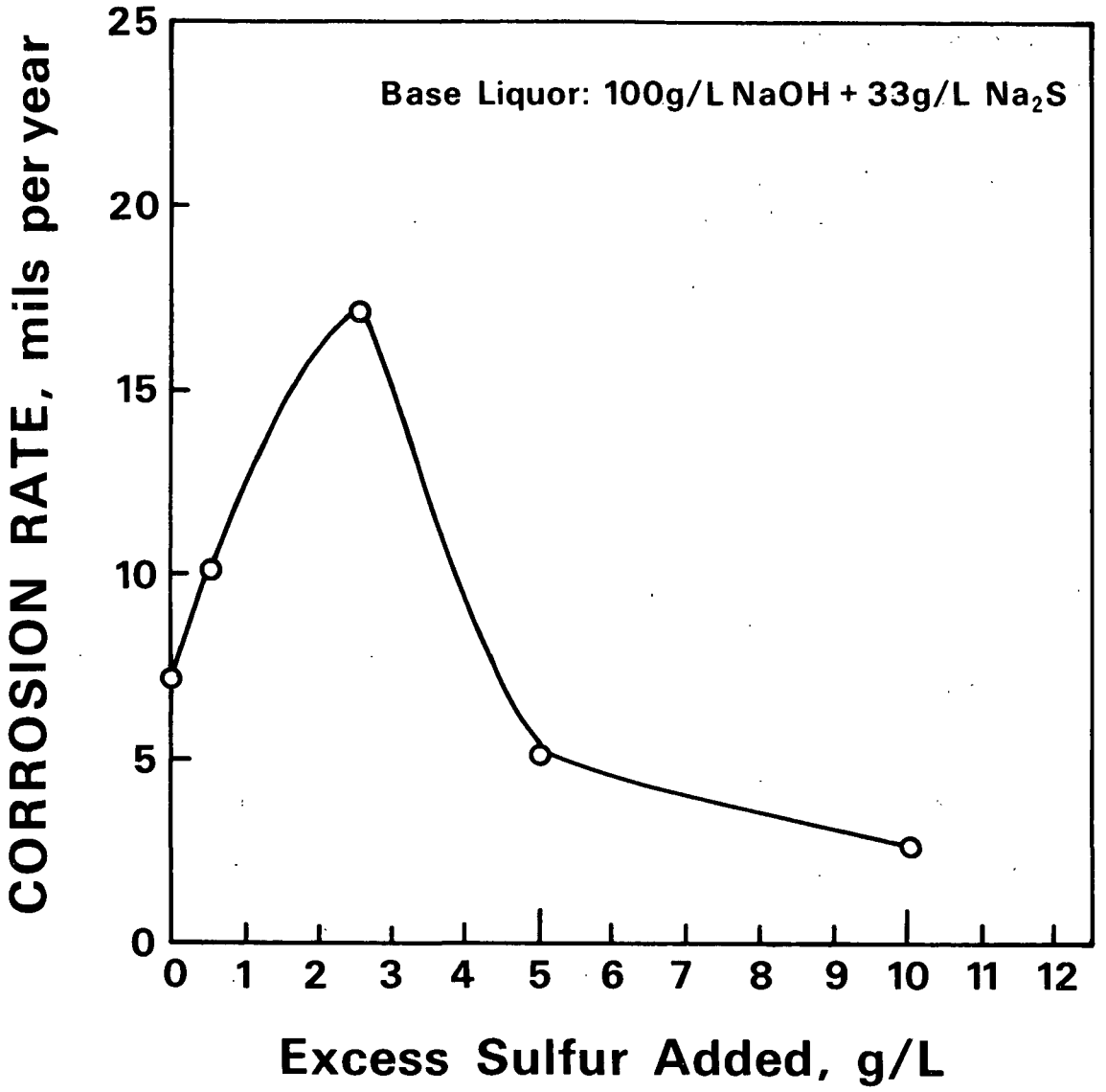

Figure 10. Effect of excess sulfur (converted substantially into Na_2S_x by reaction with Na_2S) on the corrosion rate of carbon steel in a white liquor containing 100 g/L NaOH and 33 g/L Na_2S.

Vigorous recirculation of simulated liquors significantly increased the rate of corrosion of carbon steel and elevated the rest potentials, as well. The corrosion rate in a recirculated solution containing 100 g/L NaOH and 33 g/L Na_2S was as high as 70 mpy, compared to corrosion rates on the order of 5 mpy in quiescent solutions. A similar acceleration of corrosion by recirculation of liquors was observed in solutions doped with 0.5 g/L Na_2S_2O, 5 g/L $Na_2S_2O_3$ or 0.5 g/L S^o,

where corrosion rates approaching 100 mpy were detected. Even in solutions doped with 5 g/L S^o, where protective film formation was expected and the rest potential remained at +100 mV SSS, the corrosion rate was nearly 9 mpy in the turbulent solution. Although studies of liquor velocity effects are in progress, no detailed attempts were made at this stage to investigate the relationship between liquor velocity and corrosion rate.

LINEAR POLARIZATION STUDIES

Linear polarization studies were conducted in concert with most of the weight loss studies described in the previous section, to compare the average corrosion rates determined by the two methods. The uncertainty associated with the linear polarization method originates from the uncertainty regarding the Tafel constant term, β, in Eq. (1), the oxidation state, Z, of the ions produced in the dissolution process, and the possibility of complications arising from redox reactions in the liquor or conductive film formation. The comparison of average corrosion rates obtained by weight loss and LP methods was made to resolve some of these issues.

Most of the linear polarization tests were conducted with the Petrolite Model 1010 Instrument, which provided a record of the change in current accompanying the imposition of the $\pm$ 10 mV voltage on the carbon steel electrode. When the 10 mV potential was imposed on the test electrode, the current applied by the instrument was initially very high —— more than 100 times the ultimate corrosion current —— before settling down to a constant level as shown in Fig. 11. The steady-state current was usually established within a few minutes of imposition of the 10 mV step in the voltage. The current for the corrosion rate determination was captured at the end of the cycle, well after the disappearance of any transient, non-Faradaic

effects. The shapes of the anodic and cathodic curves were similar, but the steady-state currents usually differed for the two types of test. Similarly, the shape of the current decay curve was approximately the same for tests in different liquors, and for tests in a given liquor at different times.

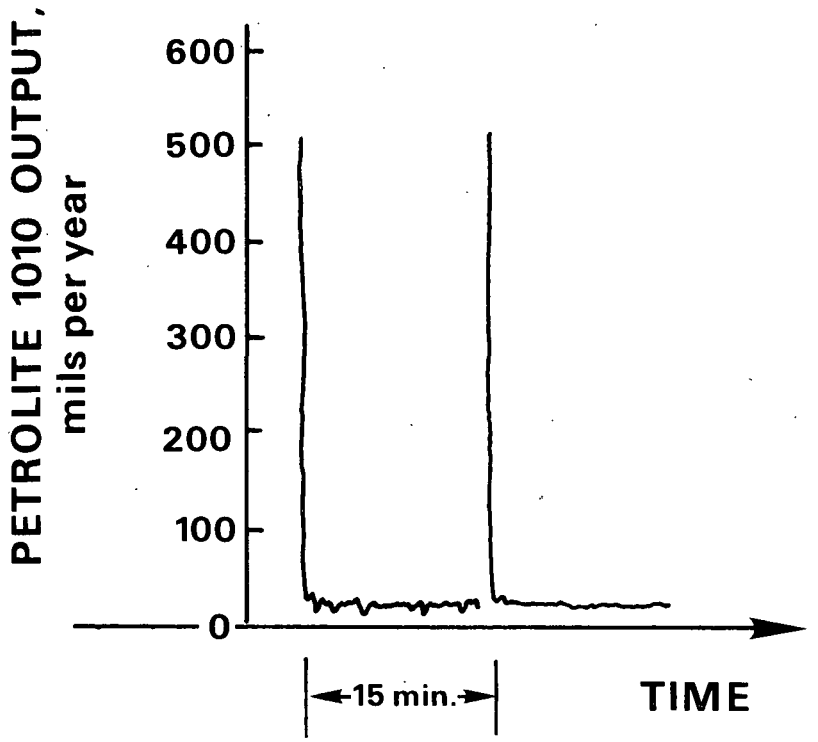

Figure 11. Current vs. time profile for a +10 mV step in the potential at the metal/liquor interface, as obtained with the Petrolite 1010.

Linear polarization tests were also conducted with a PAR 350 Corrosion Instrument by scanning the potential from -20 mV to +20 mV at a scan rate of 0.1 mV/sec. In most cases, the plot of applied current vs. applied voltage was linear and well-behaved, as shown in Fig. 12 for a test in a vigorously recirculated liquor containing 100 g/L NaOH, 33 g/L Na_2S, and 5 g/L $Na_2S_2O_3$. On occasion, however, considerable deviation from linearity was observed in the plot of ΔE vs. Δi. Examples of two common modes of nonlinear polarization behavior are shown in Fig. 13. The

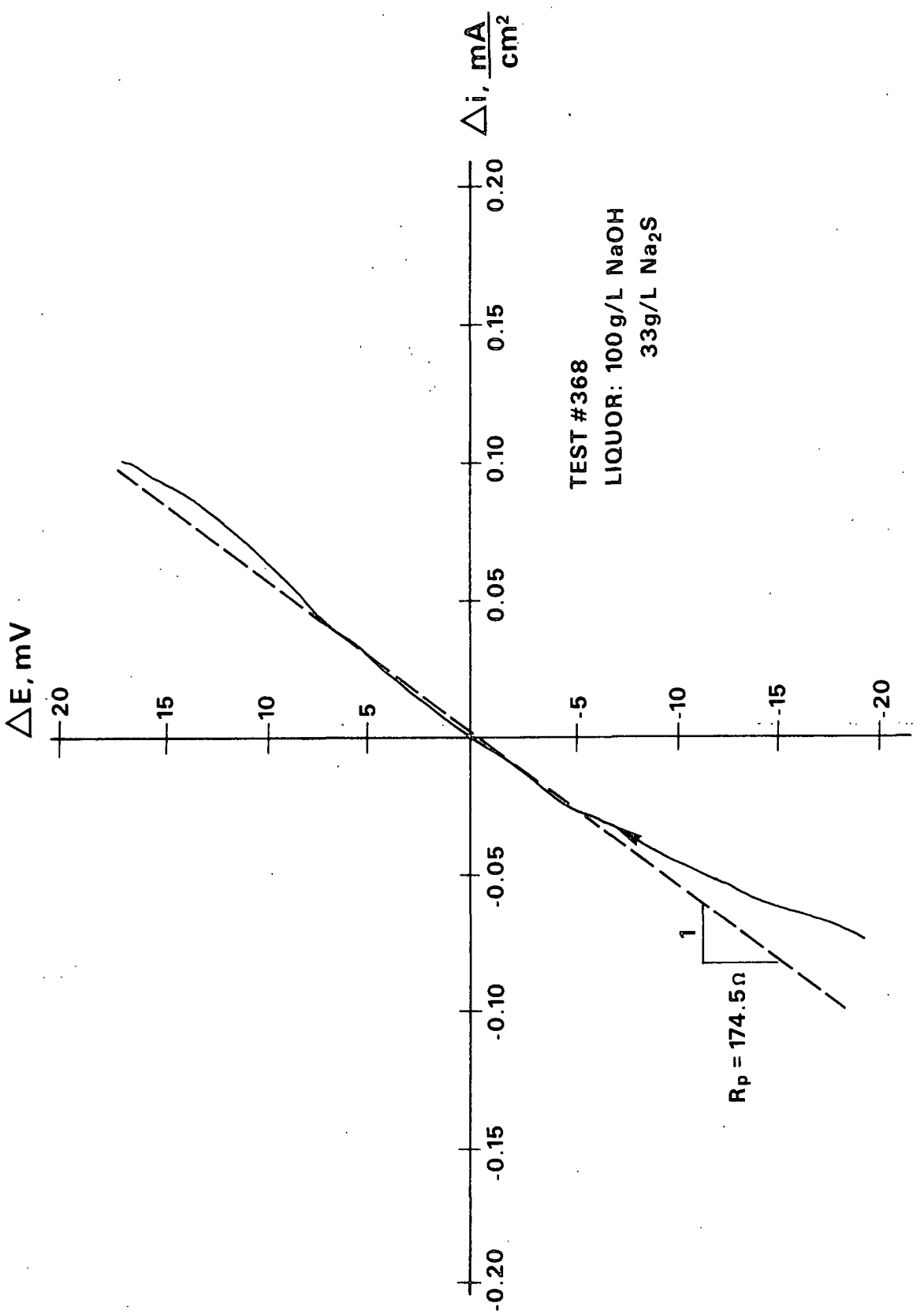

Figure 12. Current vs. voltage for a linear polarization scan from -10 mV to +10 mV scan using the PAR 350 instrument.

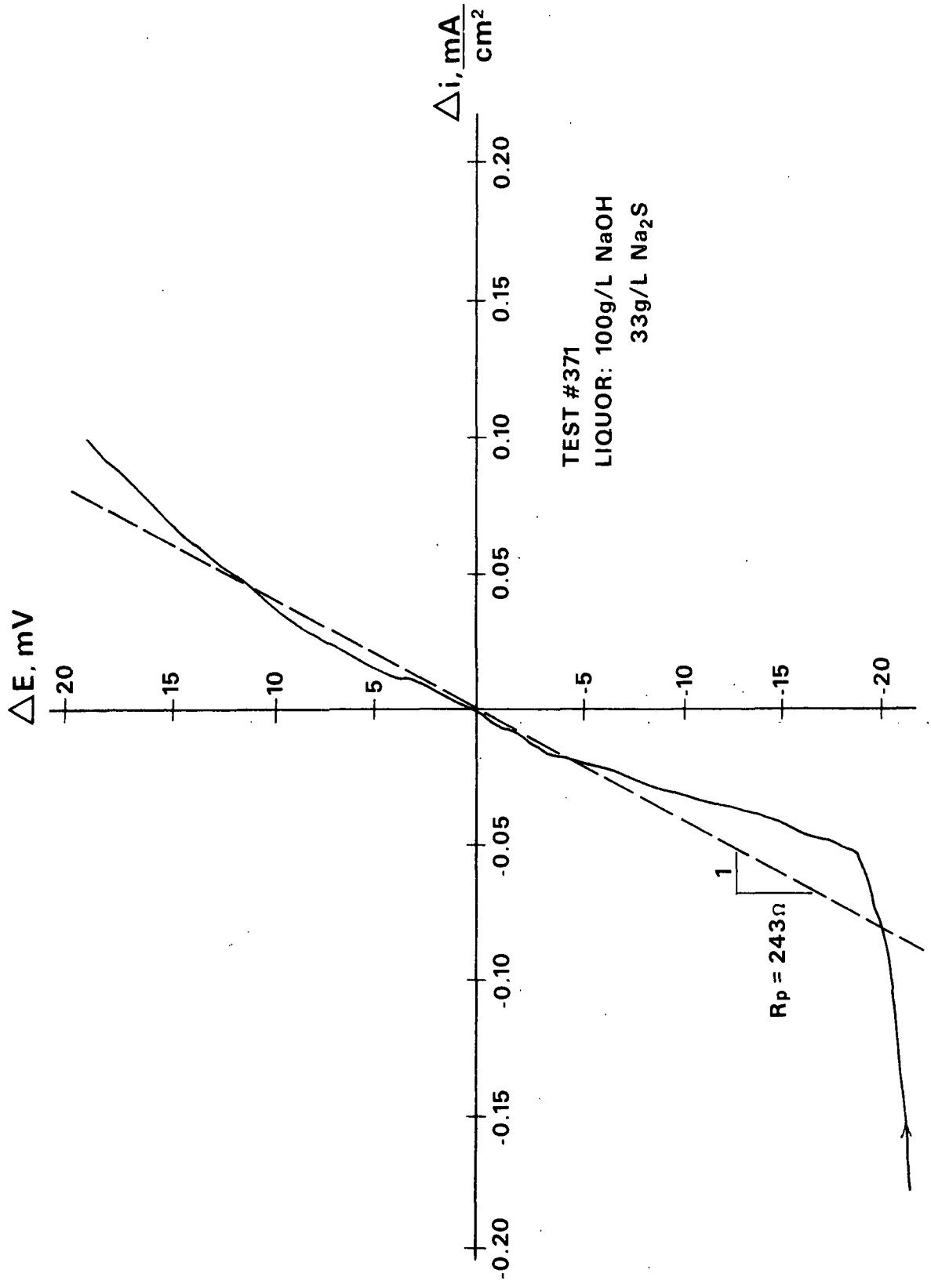

Figure 13. Examples of nonlinear responses to linear polarization scans on the PAR 350 instrument. Scan direction is from -20 mV to +20 mV with respect to E_{corr}.

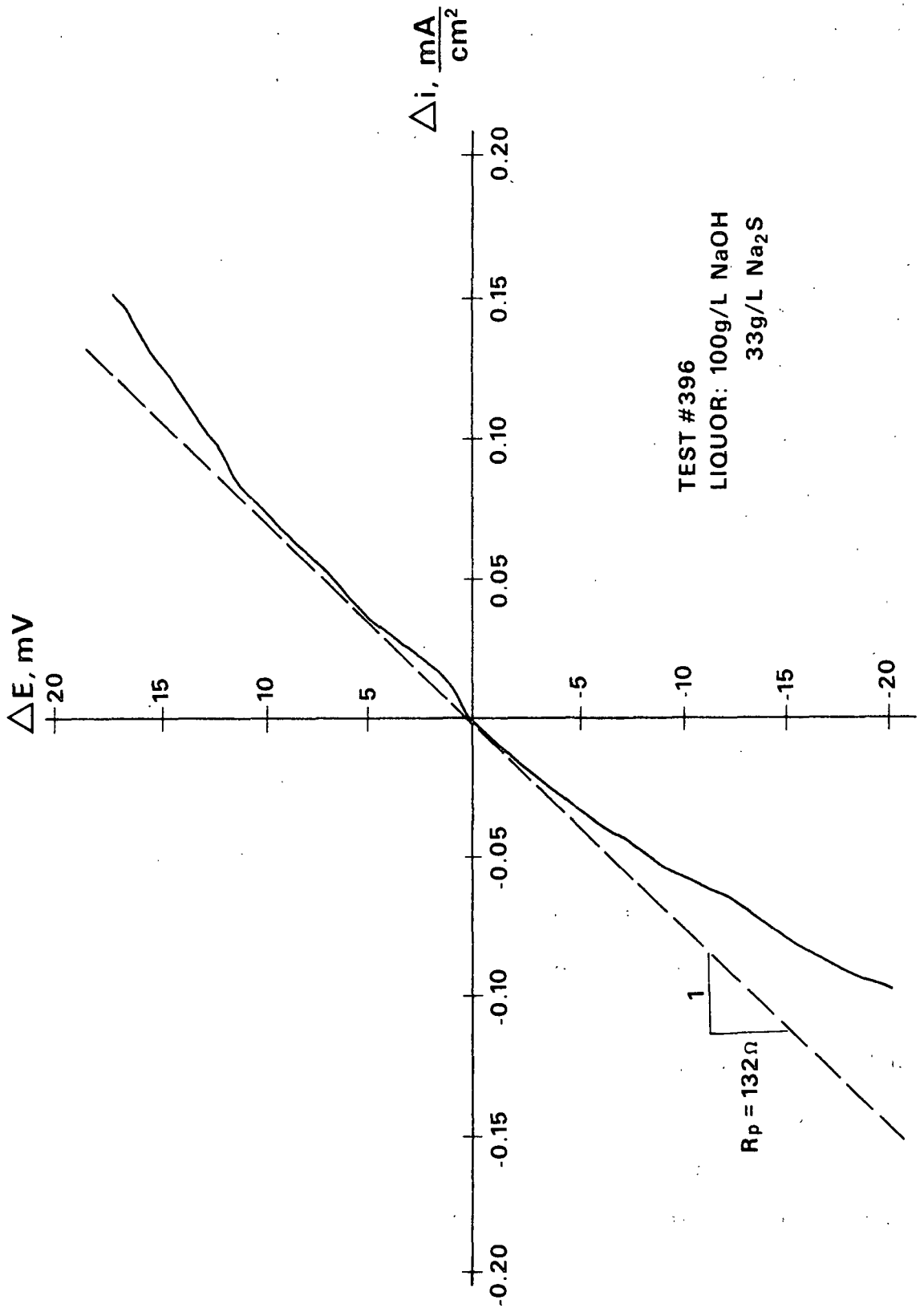

Figure 13. Examples of nonlinear responses to linear polarization scans on the PAR 350 instrument. Scan direction is from −20 mV to +20 mV with respect to E_{corr}.

high cathodic currents shown in Fig. 13A are apparently the result of non-Faradaic charging events similar to those observed at the start of the Petrolite scans. The second type of the nonlinear response to polarization, shown in Fig. 13B, was associated with an instability in the rest potential, where a 10 mV polarization caused a permanent shift in the rest potential while the potential was being scanned. The reasons for this occasional instability of the open circuit potential are not known.

In general, the agreement between the corrosion rates measured with the PAR 350 and the Petrolite 1010 instruments was reasonably good, provided the (β/Z) value of the Petrolite 1010 instrument was also used in the PAR 350 calculation.

The corrosion rates resulting from the Petrolite 1010 tests were in good qualitative agreement with the corrosion behavior reported for the weight loss tests in the previous section. The corrosion rate was high immediately after immersion, as shown for a typical case in Fig. 14, but decreased with increasing exposure time to some lower steady-state corrosion rate. In some tests, particularly those marked by high corrosion rates and wholesale delamination of corrosion product films, the LP measurements revealed several peaks in the corrosion rate during the course of a test. Moreover, as shown in Fig. 15, additions of active species (e.g., $Na_2S_2O_3$) to a test cell in midtest resulted in an abrupt increase in the rate of corrosion that was subsequently verified as real by weight loss measurements. The final item demonstrating qualitative agreement between actual corrosion rates and those measured by the LP method was the similarity of LP and weight loss results in various liquors. LP tests in solutions causing severe weight loss generally showed high corrosion rates and, conversely, LP tests in solutions producing low corrosion weight loss also show low corrosion rates. Thus, with a few exceptions discussed below, the corrosion rates measured by LP methods using the Petrolite 1010

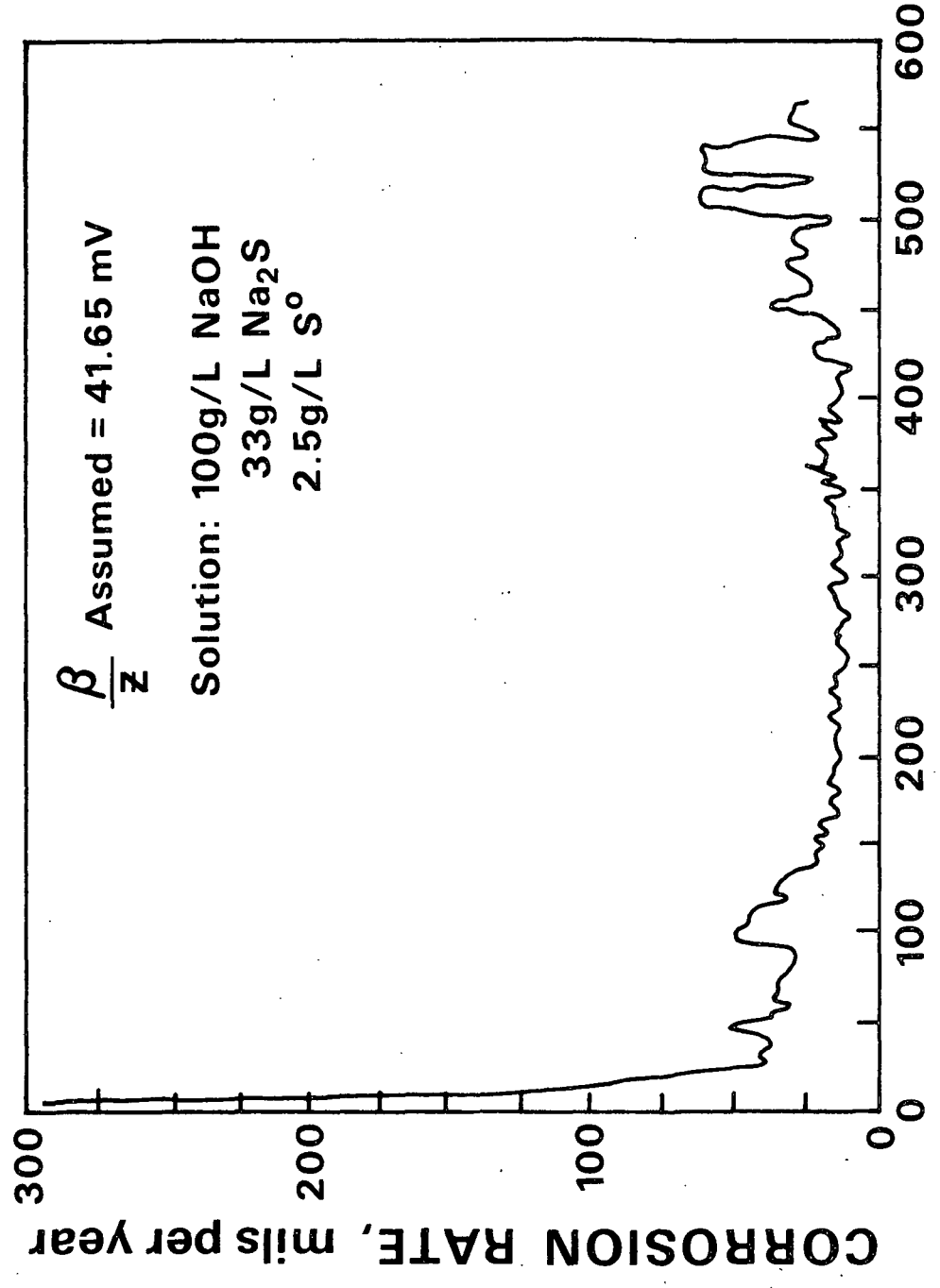

Figure 14. Examples of changes in corrosion rate during exposure of carbon steel to white liquor, as measured with the Model 1010. Data shown is as-received from the instrument, with no correction factor applied.

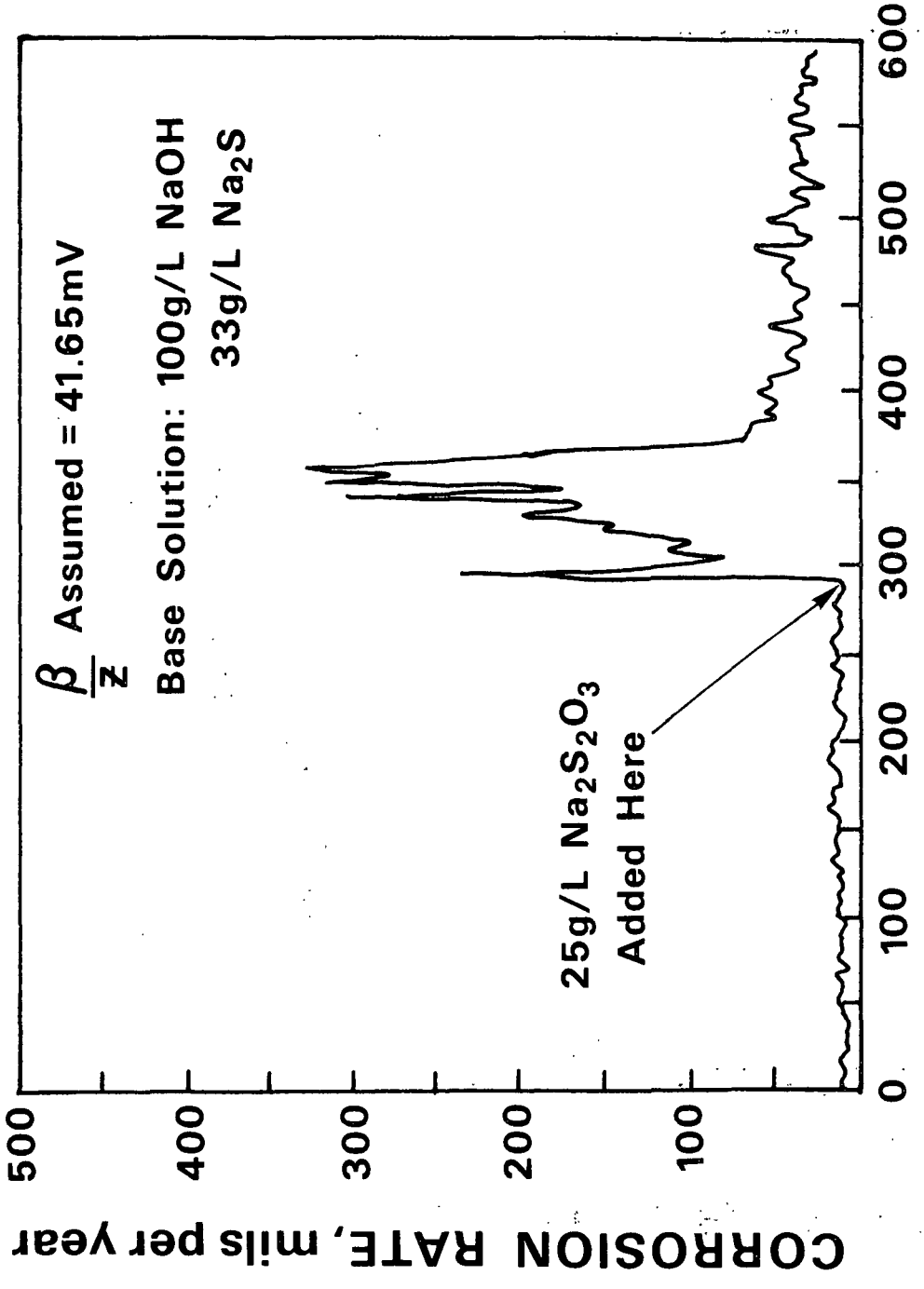

Figure 15. Transient and steady-state increases in corrosion rate caused by an addition of 25 g/L $Na_2S_2O_3$ to a solution containing 100 g/L NaOH and 33 g/L Na_2S.

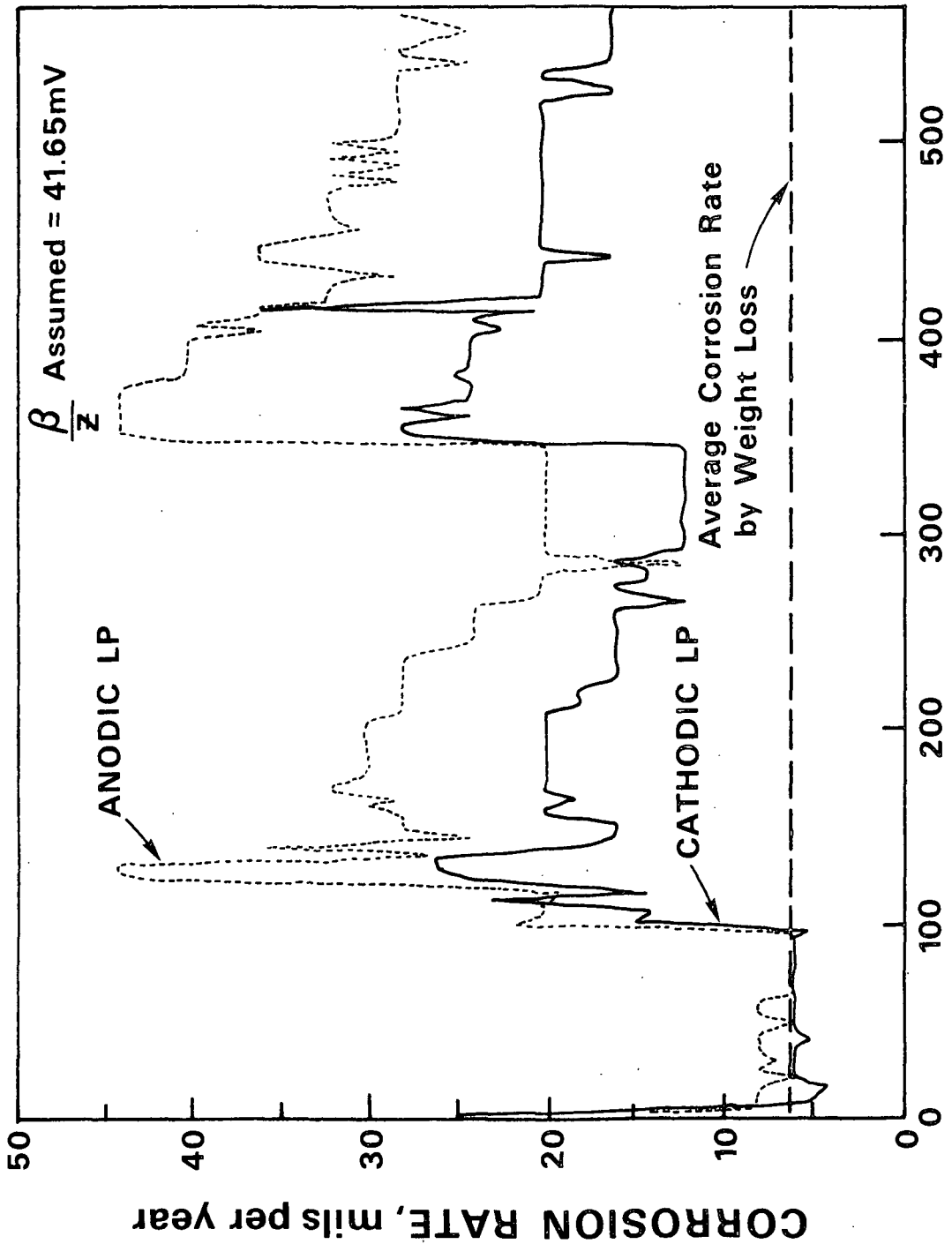

Figure 16. A comparison of linear polarization results (anodic and cathodic) from the Petrolite 1010 instrument with average weight loss results. No correction is made in as-received results from the instrument.

instrument were qualitatively responsive to the actual corrosion rates in simulated white liquors.

However, the average corrosion rates reported by the Petrolite instrument were numerically higher than those inferred from weight loss measurements. Furthermore, the corrosion rates determined by anodic (+10 mV) polarization were somewhat higher than those measured by cathodic (-10 mV) polarization, and anodic LP measurements were consequently in greater error. The corrosion rates determined by anodic and cathodic LP measurements are compared in Fig. 16 with the average corrosion rate determined by weight loss measurement. This test was conducted in a stagnant liquor containing 100 g/L NaOH and 33 g/L Na_2S. Without any correction for the β and Z constants inherent in the Petrolite instrument, the average corrosion rates determined by LP measurements were considerably higher than the average weight loss measurements would indicate. The average corrosion rates determined by LP measurements and weight-loss measurements in stagnant liquors are compared in Table III for several tests in simulated white liquors. The average linear polarization data taken directly from the Petrolite instrument are seen to be high by a factor of two, except in polysulfide-doped solutions where the differences are larger. The qualitative trends of the LP data are generally correct, in that higher levels of corrosion are accompanied by higher rates of corrosion in LP measurements.

Also shown in Table III are the values of $(\beta/Z)^*$ required to bring the averaged anodic and cathodic LP rates into agreement with the actual weight loss data. The values of β and Z inherent in the Petrolite instrument are 83.3 mV and 2, respectively, so that (β/Z) in the Petrolite instrument was initially set at 41.65 mV. Values of $(\beta/Z)^*$ are in the range 16.5 to 24.0 mV for the range of stagnant liquors containing less than 5 g/L S^o as polysulfide. For solutions doped with 5 or

10 g/L of S^o, the actual corrosion rate was quite low, yet the anodic and cathodic linear polarization measurements erroneously indicated a high rate of corrosion. The $(\beta/Z)^*$ values required to bring the LP and weight loss data into agreement are unrealistic —— less than 10 mV.

TABLE III

COMPARISON OF AVERAGE CORROSION RATES MEASURED BY LINEAR POLARIZATION AND WEIGHT LOSS. (STAGNANT SOLUTIONS.)

Environment	Recirculation	Total Exposure Time, hr	Weight Loss, mpy	Anodic LP[a], mpy	Cathodic LP[a], mpy	$(\beta/Z)^*$, mV
Ref.	No	568(472)	7(7)[b]	24(25)	17(17)	14.2(13.9)
Ref. + 2.4 g/L $Na_2S_2O_3$	No	568(472)	20(12)	51(31)	40(28)	18.3(16.9)
Ref. + 5.0 g/L $Na_2S_2O_3$	No	568(472)	18(18)	48(48)	38(38)	17.4(17.4)
Ref. + 25 g/L $Na_2S_2O_3$	No	568(472)	28(25)	72(63)	69(56)	16.5(17.5)
Ref. + 0.5 g/L S^o	No	568	10	23	18	20.3
Ref. + 2.5 g/L S^o	No	568	17	30	29	24.0
Ref. + 5 g/L S^o	No	568	5	22	21	9.7
Ref. + 10 g/L S^o	No	568	2.5	36	36	2.9

[a] (β/Z) = 41.65 mV.
[b] ( ) = Indicates test results for air saturated solutions. All others are deaerated.

Anodic and cathodic polarization curves were determined to estimate the actual Tafel slopes for carbon steel exposed to various simulated liquors, to assess whether a $(\beta/Z)^*$ value of approximately 18 mV is consistent with actual Tafel behavior. The anodic and cathodic polarization curves typically exhibited Tafel behavior (linearity of E vs. log i) when virgin steel surfaces were exposed to the liquor and the polarization curves were run soon after immersion when the open circuit potential stabilized. A pair of representative polarization curves are shown

in Fig. 17. It is seen that the extent of the straight line Tafel portion of the anodic curve is shortened considerably by the onset of passivity, but the length is generally sufficient to estimate the slope and obtain β_a. The extent of Tafel-like behavior during cathodic polarization is greater and β_c is more easily determined. Considerable electrical noise was encountered at the open circuit potential because the polarization curves were taken within an hour of electrode immersion. Table IV shows the measured Tafel slopes and the corresponding β/Z values determined with Eq. (3) and assuming Z = 2. The average anodic Tafel slope in these simulated liquors was 49 mV with a standard deviation of 11.2 mV over the range of compositions examined thus far. The average cathodic Tafel slope was 118 mV with a standard deviation of 34 mV. Using the average values of β_a and β_c, the value of the constant, β, is 34.6 mV. For Z = 2, (β/Z) is 17.3 mV, which agrees well with the $(\beta/Z)^*$ values required to bring the LP results into agreement with the weight loss results, as shown in Table IV.

Thus, it appears that the (β/Z) value inherent in the Petrolite 1010 is too large and results obtained with this instrument (or any other instrument for which β/Z is not equal to 18) must be adjusted to obtain accurate corrosion rate measurements in stagnant white liquor. The adjustment is a simple one if the (β/Z) constant for the linear polarization instrument, is known. The actual corrosion rate is given by

$$\text{Corrosion Rate (Actual)} = \text{Corrosion Rate (Measured)} \frac{(18\ \text{mV})}{(\beta/Z)_{\text{instr.}}} \qquad (10)$$

For the Petrolite instrument, the correction factor is approximately 0.43 (or 18 mV/41.65 mV). For other instruments, the $(\beta/Z)_{\text{instr}}$ value to be used in Eq. 10 would have to be obtained from the instrument vendor.

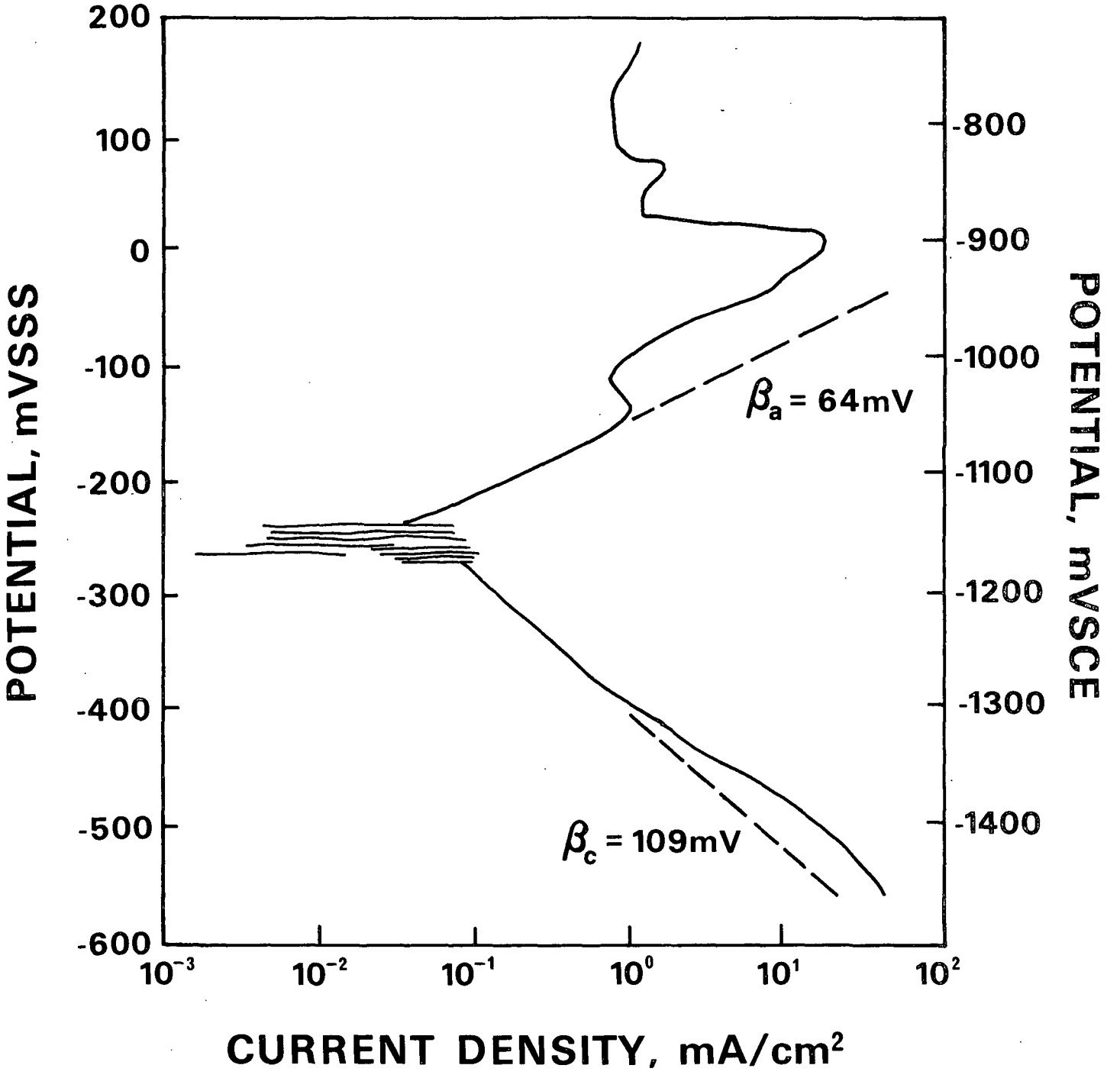

Figure 17. Anodic and cathodic polarization curves showing apparent Tafel slopes in a typical simulated liquor.

TABLE IV

MEASURED TAFEL SLOPES AND CALCULATED (β/Z) FACTORS FOR CARBON STEEL EXPOSED TO SEVERAL SIMULATED LIQUORS

Solution Composition				
NaOH, g/L	Na_2S, g/L	β_a, mV	β_c, mV	β, mV
60	15	53	98	34.4
60	20	56	94	35.1
60	25	58	101	36.8
60	30	53	98	34.4
60	35	56	101	36.0
60	40	53	117	36.5
80	25	48	109	36.0
80	40	64	109	40.3
100	15	56	105	36.5
100	20	56	110	37.1
100	25	50	150	37.5
100	30	46	130	34.0
100	35	28	84	21.0
120	10	34	98	25.0
120	25	48	235	39.0
140	10	34	134	27.0
140	15	68	105	41.0
140	20	31	144	25.5
	Average	49	118	34.6

As shown in Table III, the LP results indicate a high rate of corrosion is occurring in liquors containing high levels of polysulfide, whereas the weight loss measurements show that carbon steel is passivated in these solutions and the corrosion rate is actually low. The discrepancy appears to be a consequence of oxidation of liquor species on a nearly inert, passivated carbon steel surface. Once passivated, the carbon steel assumes nearly the same potential as the redox potential on gold or stainless steel —— approximately +100 to +150 mV SSS. This suggests that the mixed potential on passivated carbon steel is established by the same redox reactions that establish the rest potential on gold.

Since the anomalies in LP measurement occur only in polysulfide-rich solutions, it is reasonable to assume that polysulfide is involved in the redox reactions causing the error. The most likely redox reaction is the one given in Eq. (9) involving $S^{=}/S_2^{=}$ reactions and this is supported by several observations. For example, maintaining the potential of either gold or passivated steel electrodes above the usual redox potential (e.g., +150 mv SSS) by potentiostatic means will produce the characteristic yellow color of the polysulfide in the liquors —— convincing evidence that the oxidation reaction involves formation of polysulfide species. Conversely, the yellow color of a polysulfide doped liquor can be expunged if the host electrode is held at a potential slightly below 100 mV SSS. This evidence strongly suggests that the redox reaction on steel at +100 mV SSS is the $S^{=}/S_2^{=}$ couple, and the LP measurement at the +100 mV SSS potential is largely a measure of the exchange current density for this redox couple. Consequently, LP measurements in white liquors should be disregarded when the rest potential of the passivated carbon steel is in the vicinity of +100 mV SSS. Fortunately, the corrosion rate at this potential can be assumed to be negligible because of the protection offered by the passivating film.

An argument based on Tafel slope extrapolation can be used to show that liquor oxidation contributes very little to the apparent corrosion rate measured by LP techniques at active potentials of ~ -240 mV SSS. The Tafel slopes for the anodic reaction above +100 mV are very similar for gold, passivated iron, and stainless steel, but the exchange current density differs from specimen to specimen and material to material. If it is assumed that the gold electrode surface provides an upper limit to the rate of the anodic reaction because it is noble and film-free, the rate of liquor oxidation on carbon steel surfaces will always be below that

observed on gold at any potential. Measurements of the Tafel slope for the $2S^{=} \longrightarrow S_2^{=} + 2e^{-}$ reaction on gold fall generally parallel to, and within, the solid lines bounding the solid-lined area of Fig. 18. Back-extrapolation of this zone of Tafel behavior at high potentials to lower potentials provides a means of estimating an upper limit to the rate of liquor oxidation at any potential below 100 mV SSS. Thus, the dashed lines bounding the extrapolated cross-hatched area will mark upper limits on the current density due to liquor oxidation and, by extension, mark an upper limit to the contribution of liquor oxidation to the LP measurement of the corrosion rate any any potential. Converting the current density to an equivalent corrosion rate on iron (assuming Z = 2), it is seen that liquor oxidation will contribute less than 1 mpy to the LP measurement of corrosion rates at a potential of -240 mV SSS. At +100 mV, however, the upper limit of the corrosion current on gold implies an upper limit on the equivalent corrosion rate measured on gold of 100 mpy. This calculation demonstrates the origins of errors in LP measurements at high potentials (~ 100 mV SSS) and the reasons for disappearance of errors due to liquor oxidation at lower potentials, as documented in Table IV.

In vigorously recirculated solutions, the (β/Z) constant required to bring the LP measurements into agreement with the weight loss results is not 18 mV as was observed in similar but stagnant liquors. As shown in Table V, the corrosion rates observed in the vigorously recirculated solutions were also much larger than those observed in the stagnant liquors, with the exception of the passive steel in the solution doped with 5 g/L S^{o}. Attempts to measure the actual Tafel slopes in the vigorously recirculated solutions usually produced polarization curves without significant Tafel regions. In a few cases where the Tafel slopes could be determined, both β_c and β_a were in the range 130 to 350 mV. The higher apparent values for β_a and β_c under recirculation conditions are not consistent with the

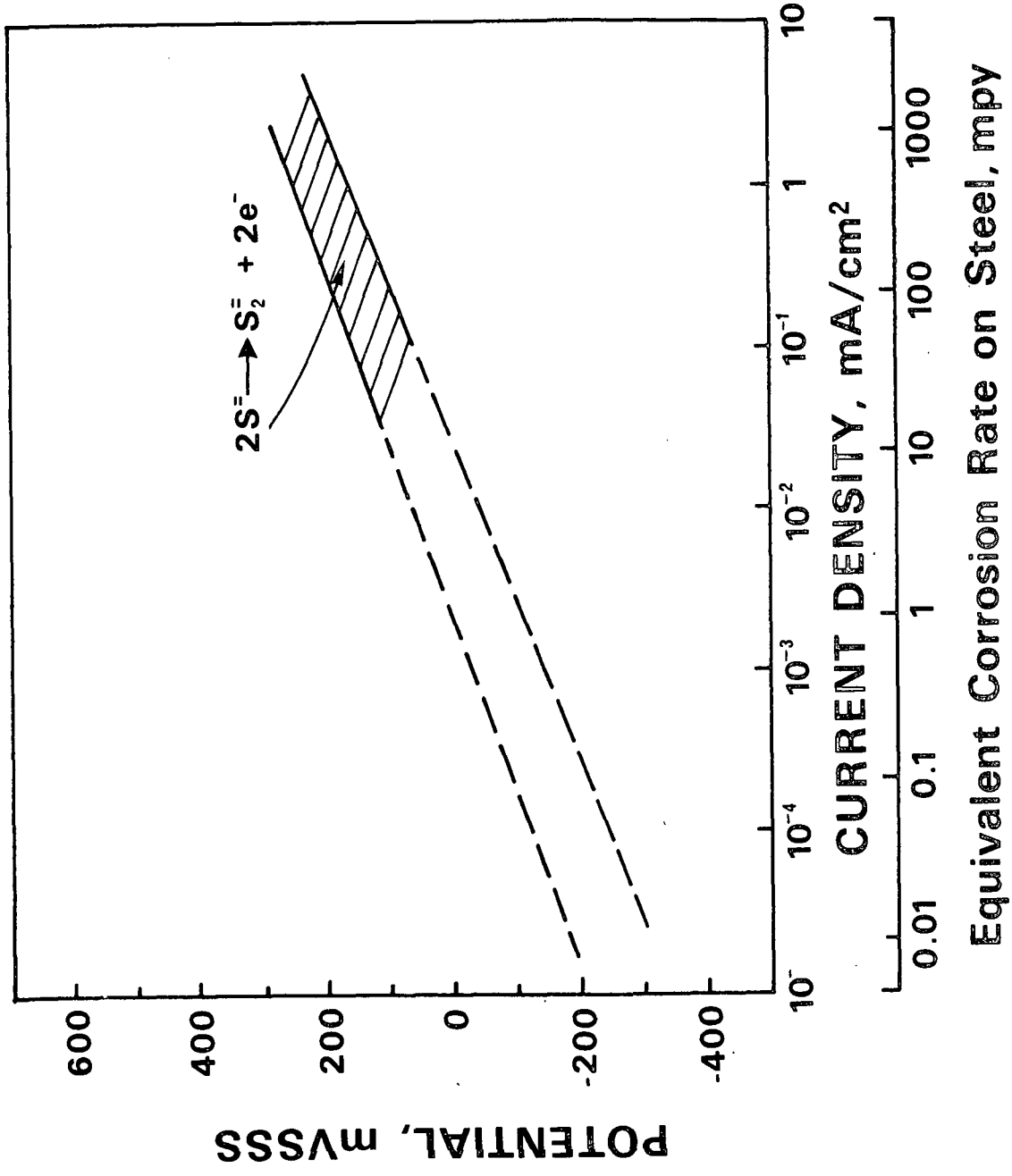

Figure 18. Current due to anodic reaction involving liquor oxidation as a function of potential. Extrapolation to lower potentials suggests that liquor oxidation contributes little to apparent corrosion rate at -240 mV SSS, as shown by equivalent scale in mpy of corrosion of iron.

electrochemical theory of dissolution under activation polarization conditions, and further work is planned to resolve this question. The higher values of Tafel slope constants would be consistent with the higher values of $(\beta/Z)^*$ required to bring the LP results into agreement with the weight loss results, however. If β_a and β_c are both 130 mV/decade and Z = 2, for example, the (β/Z) value to be applied in Eq. (1) is 32 mV. This value is closer to the $(\beta/Z)^*$ values shown in Table V, but the agreement may only be fortuitous.

TABLE V

COMPARISON OF AVERAGE CORROSION RATES MEASURED BY LINEAR POLARIZATION AND WEIGHT LOSS METHODS (VIGOROUSLY RECIRCULATED SOLUTIONS)

Environment	Recirculation	Total Exposure Time	Weight Loss	Anodic LP[a]	Cathodic LP[a]	$(\beta/Z)^*$
Ref.	Yes	900 hr	60 mpy	56 mpy	52 mpy	46.3
Ref. + 5 g/L $Na_2S_2O_3$	Yes	430	82	212	153	18.7
Ref. + 0.5 g/L S^o	Yes	490	61	82	59	36.0
Ref. + 5 g/L S^o	Yes	530	7	32	32	5.4

[a] $(\beta/Z) = 41.65$ mV.

Although the analysis of corrosion product structures by x-ray diffraction studies have not been completed, some clues have been obtained regarding the oxidation state of the iron dissolved from the steel. The principal corrosion product obtained from the surface of coupons exposed to liquors containing only NaOH and Na_2S appears to be Mackinawite, an iron-rich non-stoichiometric form of FeS. In this case, an oxidation number of 2 is appropriate and is in agreement with the $(\beta/Z)^*$ values described above. In solutions containing a high level of $Na_2S_2O_3$, the corrosion product is a greenish-black, cohesive film identified as $NaFeS_2$, which spalls from the surface of the specimen in large sheets. The oxidation state of

iron in this compound is not known, but may be +3 if sulfur remains in the -2 valence state. In several cases, particularly in cases where the liquor contained an abundance of Na_2S_x, the corrosion products were sulfur-rich and largely amorphous. These deposits may be amorphous sulfur which is created by disproportionation of polysulfides as an intermediate step in the reduction of polysulfide,

$$S_2^{=} \longrightarrow S^{=} + S^{o},$$

or as a consequence of partial oxidation of sulfide via

$$S^{=} \longrightarrow S^{o} + 2e^{-} \quad .$$

Precipitates of nearly pure sulfur have been detected on the surface of steel coupons exposed to polysulfide-enriched solutions, as shown in the scanning electron micrograph of Fig. 19. Further investigation is required to correlate the corrosion products and the composition of the white liquor.

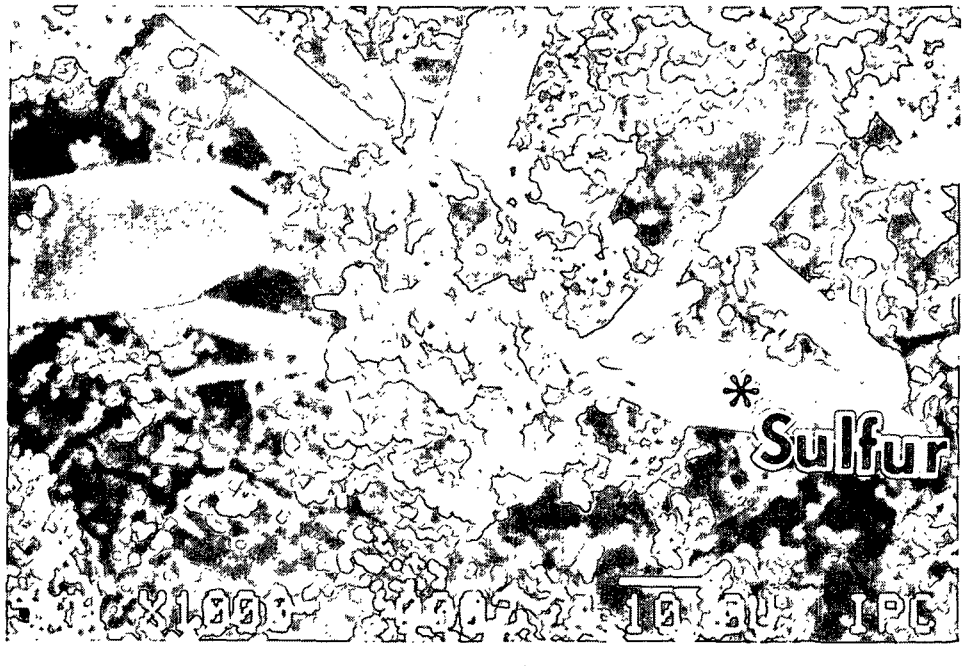

Figure 19. Scanning electron micrograph of sulfur deposits in the corrosion deposits on a corroded sample. Energy dispersive x-ray analysis at the indicated point showed sulfur as the only constituent.

DISCUSSION

EFFECTS OF DISSOLVED CONSTITUENTS ON CORROSION RATE

The present observations of accelerated corrosion of carbon steel in the presence of thiosulfates and dilute polysulfides confirm early reports by several investigators (8,14-16). The role of thiosulfate was first noted by Stockman and Ruus (14-15) who reported a dramatic increase in corrosion rate of steel exposed during actual cooking cycles in liquors doped with various amounts of thiosulfate. The strong effect of thiosulfate as an accelerator of corrosion in kraft liquors was also reported by Haegland and Roald (8). Both Uusitalo (17-18) and Hasseler (10) did not detect a large acceleration in corrosion due to additions of thiosulfate to white liquors, but their tests were of relatively short duration. Wensley and Charlton (1) determined that the corrosion rates in several actual kraft liquors containing 7-8 g/L $Na_2S_2O_3$ were about the same as the 18 mpy observed in the present study at a similar thiosulfate level.

The origins of the thiosulfate effect on corrosion rates is not well established, but Haegland and Roald (8) present evidence that the thiosulfate effect is caused by its effect on the polysulfide concentration. These authors suggest that thiosulfate additions promote the formation of polysulfide via the reaction

$$Na_2S + Na_2S_2O_3 \rightleftharpoons Na_2S_2 + Na_2SO_3.$$

The equilibrium constant for the reaction is

$$K = \frac{[Na_2SO_3]\ [Na_2S_2]}{[Na_2S]\ [Na_2S_2O_3]} = 1.6 \times 10^{-4} \qquad (11)$$

at room temperature, corresponding to formation of a dilute polysulfide solution upon addition of $Na_2S_2O_3$. As shown by Hassler (10) and several others, a dilute polysulfide solution promotes corrosion by providing an alternative to the hydrogen reduction reaction, similar to the effect of dissolved oxygen in dissolution by acids.

Although the polysulfide mechanism for the thiosulfate effect is interesting, it does not appear to be the sole source of the effect on corrosion rates. Wensley and Charlton (9) and Uusitalo (17-18) have shown, for example, that the presence of thiosulfate in white liquor significantly increases the critical current density required to achieve passivation during anodic polarization, i_{crit}. If the only effect of thiosulfate was an increase in the concentration of an oxidizing species such as polysulfide, the value of i_{crit} would be reduced, not increased. Apparently, the thiosulfate also affects the ease with which passivation can be induced on a carbon steel surface. This may be a result of formation of the iron-thiosulfate complex, which would remove Fe^{++} and/or $HFeO_2^-$ ions from the vicinity of corroding surface, thereby increasing the anodic current necessary to exceed the concentration required for precipitation of Fe_3O_4 or Fe_2O_3. As mentioned previously, the presence of $Na_2S_2O_3$ also has an effect on the nature of the corrosion product formed on the corroding metal surface, but the interaction of the film and the corrosion rate is unknown at present.

The effect of polysulfide additions on corrosion of carbon steel exposed to white liquors is a well-known consequence of the oxidizing character of the polysulfide. Ruus and Stockman (14) appear to have been the first to recognize the important role of polysulfide as a "cathodic depolarizer" during corrosion of carbon steel. As shown schematically in Fig. 20 the presence of a small amount of polysulfide

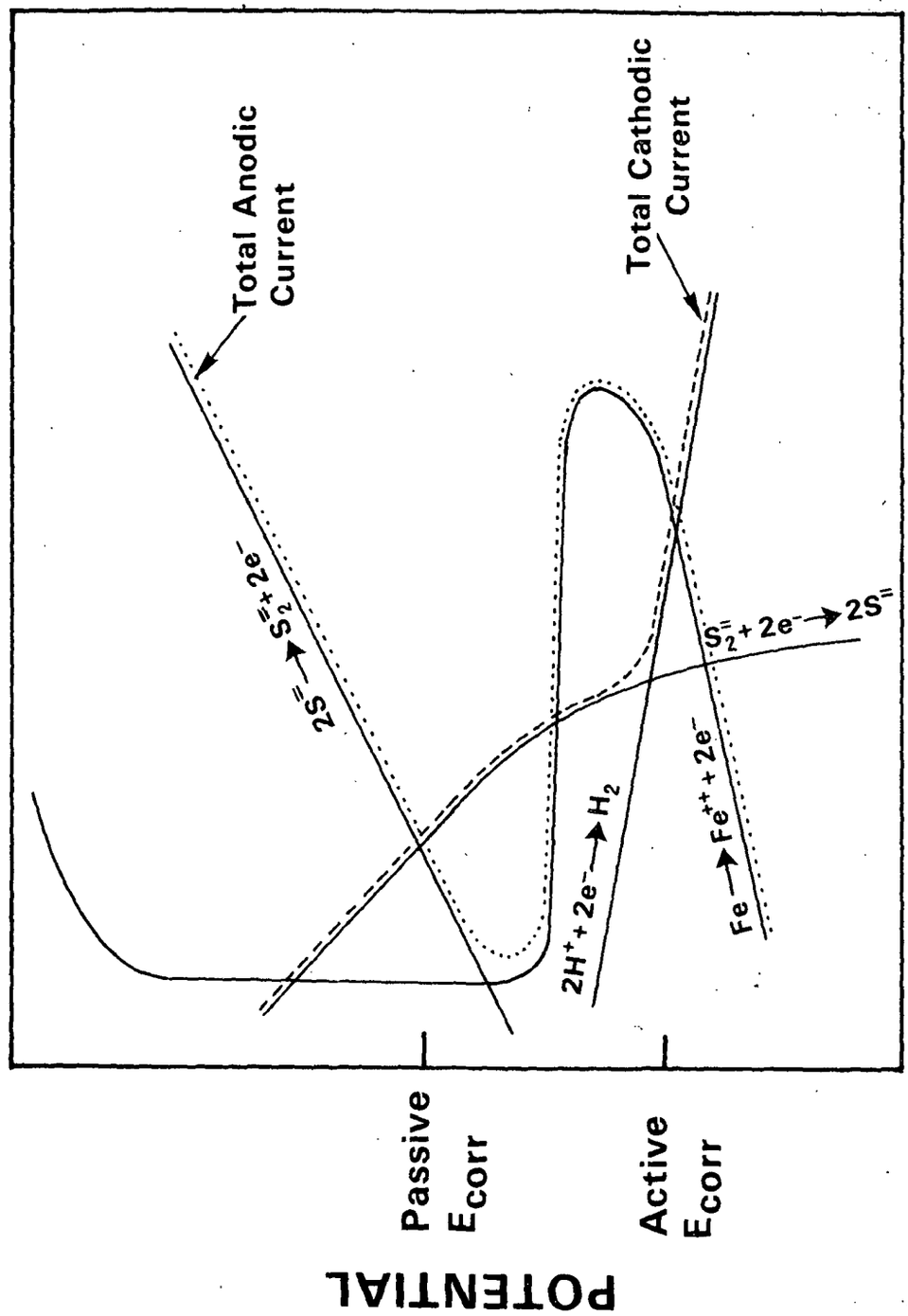

Figure 20. Schematic diagram showing the establishment of the mixed potential of carbon steel in the presence of polysulfide.

can accelerate the corrosion rate of carbon steel by providing an alternative reduction reaction for the cathodic process involved in corrosion. The hydrogen ion reduction reaction can only support a limited amount of corrosion of carbon steel because the half cell potentials of the iron dissolution reaction and the hydrogen reduction are so close in white liquor conditions. However, the existence of a second reduction reaction whose half cell potential is more noble than the hydrogen reduction reaction can increase the active corrosion rate to levels well beyond that observed in liquors without oxidants, as is often observed with dissolution of iron in air-saturated acids. Up to a certain level, the higher the concentration of Na_2S_x, the higher the rate of corrosion of carbon steel in white liquor.

When the concentration of polysulfides is great enough to provide a cathodic current equal and opposite to i_{crit}, the critical current for passivation will be available and the carbon steel will spontaneously passivate. The corrosion that occurs at the passive surface is very low —— well below the apparent passivation maintenance current observed with the anodic polarization curve because some liquor oxidation will be included in this apparent maintenance current.

The active/passive nature of the effect of polysulfide on white liquor corrosivity was also observed in the present investigation, but the corrosion acceleration caused by polysulfide was smaller than the effect of thiosulfate. The effect of polysulfide may be limited because the polysulfide contained in the small chamber will be consumed after a few days of exposure to ~30 cm^2 of carbon steel surface. Additional tests are planned to determine the rate of corrosion when carbon steel is exposed to white liquor with the same concentration of polysulfide, but with a larger reservoir of the simulated liquor.

The insignificant effect of dissolved oxygen on corrosion rate is probably a result of rapid oxidation of oxygen to form sulfoxy compounds. No attempt was made to analyze the solutions following the exposure, but Meuller (13) has shown that rapid oxidation of sulfides will occur at 90°C, with initial formation of thiosulfate, but with eventual formation of sulfite and sulfate if the oxygen supply is adequate. The kinetics of formation of thiosulfate compounds in white liquors is relatively rapid at 90°C, but the formation of sulfites and sulfates is relatively sluggish. Consequently, it is likely that the entire oxygen supply in the plenum above the liquor (and dissolved in the liquor itself) is rapidly converted to thiosulfate at the start of the exposure. The total amount of oxygen is limited, however, and a simple calculation shows that the sulfoxy reaction can reach an end point with the complete consumption of the oxygen by formation of a small amount (approximately 0.5 g/L) of $Na_2S_2O_3$. Thus, most of the exposure in "aerated" solutions was actually made in solutions that had been deaerated by formation of an insignificant amount of thiosulfate. The good agreement between the aerated and deaerated solutions is therefore not remarkable, but is a consequence of the rapid reaction of sulfide with a limited amount of available oxygen to deaerate the initially aerated solution. Increasing the available oxygen (by, for example, bubbling air through the solution) will only increase the extent of formation of sulfoxy compounds, so the effect of dissolved oxygen on cathodic processes involved in corrosion cannot be studied directly by laboratory tests involving limited quantities of liquor.

Although thiosulfate and polysulfide dissolved in white liquor can have a profound effect on the corrosion rate, the concentration of the major constituents —— sodium hydroxide and sodium sulfide —— has little effect on the overall corrosion rate. Increased concentrations of either of these constituents is deleterious

to corrosion resistance, but the effect is not very large over the range encountered in white liquors. This contradicts the prediction of Wensley and Charleton (9), Uusitalo (17-18) and others who have shown that both NaOH and Na_2S concentrations increase i_{crit} and therefore impede the formation of a passive film. An explanation of the disparity is that the carbon steels exposed in the current tests are exposed with little or no oxidant present and therefore they remain active, regardless of the magnitude of i_{crit}. Since passivation is not possible under these circumstances, the magnitude of i_{crit} has little bearing on the rate of active corrosion.

The effect of solution velocity on the rate of corrosion of carbon steel in white liquor is not entirely unexpected in view of the apparent role of surface films in the corrosion process. Of course, the ease of maintaining a protective film is known to be affected by the velocity of the electrolyte in contact with the metal surface in many metal/electrolyte systems. Indeed, Mueller (19) has shown that a large liquor velocity effect was apparent in his studies of white liquor corrosivity. The present experiment, undertaken to achieve different corrosion behavior for linear polarization testing, was too limited to justify speculation regarding the mechanism of the velocity effect.

LINEAR POLARIZATION MEASUREMENTS

The linear polarization method for measuring corrosion rates in white liquors appears to be sensitive to changes in corrosion rate caused by extended time of exposure, concentration of dissolved species, liquor velocity, and mid-test additions of corrosion accelerants. In agreement with this study and earlier work (10), the LP measurements of corrosion rate indicate a period of high corrosion at the outset of an exposure test, followed by a protracted period of corrosion at a more

or less constant rate. In general, solutions that result in high levels of corrosion as measured by weight loss measurement also produce higher corrosion rates in measurements by the linear polarization method. The exceptional case occurs in solutions containing high concentrations of polysulfide, where the actual corrosion rate is low but liquor oxidation occurring at the passive carbon steel is responsible for a high ⟶ and erroneous ⟵ corrosion rate measurement by linear polarization methods. As long as carbon steel remains active, the linear polarization method appears to be a useful diagnostic tool for monitoring the corrosivity of alkaline sulfide liquors used in kraft pulping.

However, certain ambiguities have been identified in the interpretation of the LP results obtained in white liquors. Principal among these uncertainties is the erroneously high rate of corrosion detected in high polysulfide solutions, and the corrections in the (β/Z) values to be used in the LP calculations based on Eq. (1).

In a practical application, the errors associated with liquor oxidation reactions can be discounted by simultaneous measurement of the corrosion rate and the corrosion potential. The contribution of redox reactions to the apparent corrosion rate measured by LP methods is large only when the corrosion potential rises to 100 mV SSS. Below this potential, redox reactions will contribute little. Above this potential, the carbon steel will be passivated and corrosion damage will not be a concern. Measurement of the corrosion potential during LP measurements will indicate when the metal is passivated, implying that the corrosion rate is low and LP measurements of the corrosion rate are likely to be erroneously high.

The importance of disregarding LP results on electrodes with corrosion potentials above 100 mV SSS emphasizes two practical aspects of LP measurement.

First, an accurate measurement of the carbon steel potential is a necessary step in a strategy for accurate measurement of corrosion rates. The usefulness of the silver/silver-sulfide reference electrode (5) looms large, because accurate measurement of the potential in white liquors without the SSS reference electrode will be complicated at best. The SSS electrode provides a stable reference potential without the need for the paraphernalia of the electrochemist —— salt bridges, liquid junctions, etc., —— that are beyond the reach of the average mill site study. The SSS electrode greatly facilitates the measurement of the important rest potential of the carbon steel electrode in white liquors. Second, an apparatus for LP measurement should have a three electrode configuration with capability for measurement of the rest potential of the carbon steel working electrode versus a reliable reference potential. LP instruments with the three electrode configuration (with a SSS reference electrode) will greatly facilitate the measurement of rest potential, compared to two electrode LP configurations that are available commercially. Although two electrode LP tests can be supplemented with additional monitoring of rest potential of the carbon steel electrode, the additional complexity of this approach is unattractive.

In the absence of good Tafelian behavior and readily identified states of oxidation for products of dissolution, accurate measurement of corrosion rates using the LP method requires an empirical calibration of the (β/Z) values to coincide with actual weight loss results. The optimum approach is to conduct simultaneous LP/weight loss studies in the environment of interest to determine a (β/Z) value for use in LP measurements at this site. If this approach is inconvenient or great precision is unnecessary, the use of the $(\beta/Z)^*$ value of 18 mV determined in the present study would be justified if the white liquors at the site of testing is relatively static.

Whether the empirical $(\beta/z)^*$ values discovered in these studies can be unequivocally related to the kinetics of the anodic and cathodic processes occurring on the carbon steel electrodes remains to be seen. Good agreement between empirical and theoretical (β/Z) values was obtained in limited tests, based on Tafel slope measurements in a few quiescent liquors and an assumption that the charge transfer reaction involves two electrons. Whether this agreement extends to the general case of white liquor corrosivity will require results of further tests which are currently underway. Rationalization of the apparent effects of liquor velocity on the (β/Z) must also await the results of further study.

Efforts are also underway to examine the validity of the three point method (20) of LP measurement for corrosion rate determination in white liquor. With this method, a sensing electrode is subjected to a three-step polarization beyond the linear range, ΔE, $2\Delta E$, and $3\Delta E$, and the corresponding applied current densities, Δi_1, Δi_2, and Δi_3, are measured at each potential. Three equations in three unknowns (β_a, β_c, and the corrosion current, i_{corr}) are generated by inserting each of the three $\Delta E/\Delta i$ pairs in the Stern-Geary equation, which are solved by simultaneous methods. This approach has the value of a simultaneous determination of all three unknowns in the corrosion rate equation in a single measurement, with an independent measurement of β_a and β_c. Early results are promising in that the β_a and β_c values obtained by the three point method appear to coincide with those reported here.

CONCLUSIONS

The results of this study justify the following conclusions.

1. Corrosion of carbon steel by simulated white liquors is increased by high levels of thiosulfate and low-to-moderate levels of polysulfide; the concentration of sodium hydroxide or sodium sulfide has little effect on the corrosion rate over the range encountered in white liquor.

2. Linear polarization measurements with commercial instrumentation generally provide a good qualitative indication of the corrosivity of alkaline sulfide solutions when carbon steel is undergoing active corrosion, but empirical calibration of the LP results is necessary.

3. Linear polarization measurements will be in error when the carbon steel is passivated, as indicated by a rest potential of carbon steel of approximately 100 mV SSS. Corrosion rates of carbon steel measured at this potential are low and generally insignificant. The errors in linear polarization at this potential are apparently a result of contributions by redox reactions occurring in the liquor.

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THE INSTITUTE OF PAPER CHEMISTRY

Ronald A. Yeske
Senior Research Associate
Engineering Materials/
Corrosion Section
Engineering Division

Clyde H. Sprague
Director
Engineering Division

APPENDIX I

ELECTROCHEMICAL THEORY OF LINEAR POLARIZATION MEASUREMENTS

The measurement of corrosion rates by the linear polarization method is based on a mathematical model of the oxidation and reduction processes occurring on the surface of a corroding metal. The treatment follows that first developed by Stern and Geary (2).

THEORETICAL ASPECTS

When corrosion occurs on a metal surface, at least two reactions are involved. The familiar reaction is an oxidation of the metal to form dissolved ions with removal of some of the electrons from the metal atom. A typical oxidation reaction would be

$$Fe \longrightarrow Fe^{++} + 2e^{-} \qquad (12)$$

The formation of dissolved Fe^{++} ions leads to visible wastage of the metal, so this reaction alone is often held responsible for corrosion. However, dissolution would not occur as shown in Eq. (1) unless there was some process available to consume the free electrons created during metal dissolution. If these electrons were not consumed in some fashion, but were left behind by the dissolved metal ions, an enormous charge would build up on the metal that would eventually stifle the dissolution reaction. Since corrosion does proceed under some conditions, some reaction must be capable of removing the electrons created. This electron-consuming reaction is called a reduction, and two common reduction reactions are shown below.

$$2H^{+} + 2e^{-} \longrightarrow H_2 \qquad (13)$$

$$O_2 + 4H_2O + 4e^{-} \longrightarrow 4OH^{-} \qquad (14)$$

The first reduction reaction is the familiar evolution of hydrogen that occurs when metals dissolve in acids; the second is less well-known, but is important in everyday corrosion of iron and steel. As shown in Fig. 21, both oxidation and reduction must occur at the same rate on the metal surface for corrosion to proceed.

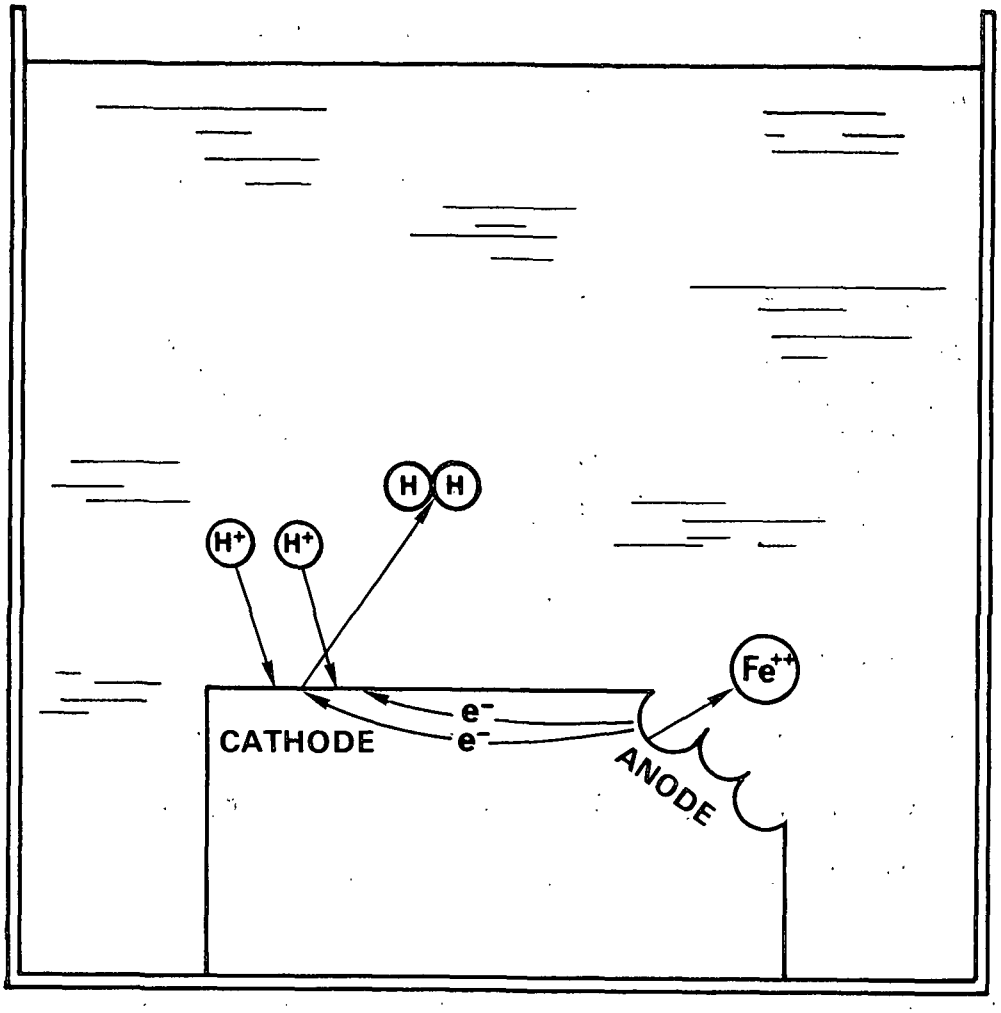
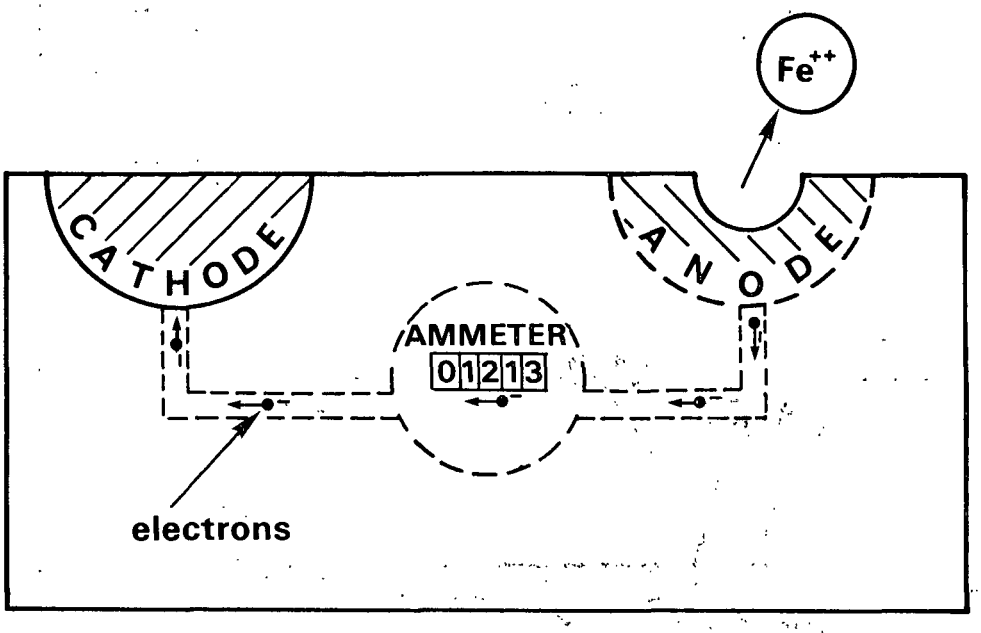


Figure 21. Corrosion occurs as a result of anodic (dissolution) and cathodic processes occurring simultaneously on a metal surface.

Measurement of the corrosion rate would be a simple matter if the electrons created at the anode were forced to pass through an imaginary ammeter on their way to being consumed at the cathode, as shown in Fig. 22. One would merely count electrons and calculate the corresponding number of metal ions created. In reality,

such an ammeter is ludicrous, particularly since innumerable anodes and cathodes exist on a corroding metal, and they are constantly shifting position. Some indirect method of assessing the current between anodes and cathodes is essential if the corrosion current is to be determined. This section deals with two simple, indirect methods to determine the number of electrons passing from local anodes to cathodes and, by extension, to determine the rate of corrosion.



An Imaginary Ammeter to Measure the Corrosion Current, i_{corr}

Figure 22. An imaginary ammeter to determine the electron current flowing between local anodes and cathodes, as the basis for estimating the number of metal ions produced by corrosion.

Every metal immersed in an electrolyte establishes a voltage at the metal/electrolyte interface which can be measured using the apparatus shown in Fig. 23. The reference electrode is a device that maintains the same voltage during immersion, regardless of the electrolyte used; it serves as a handy benchmark connected to the low (-) terminal of the voltmeter. Measured voltages are usually

referred to the reference electrode used, as, for example, -700 mV *vs.* the saturated Calomel reference electrode —— or -700 mV SCE. The potential that is spontaneously achieved by a metal in an electrolyte is called the *corrosion potential*, E_{corr}.

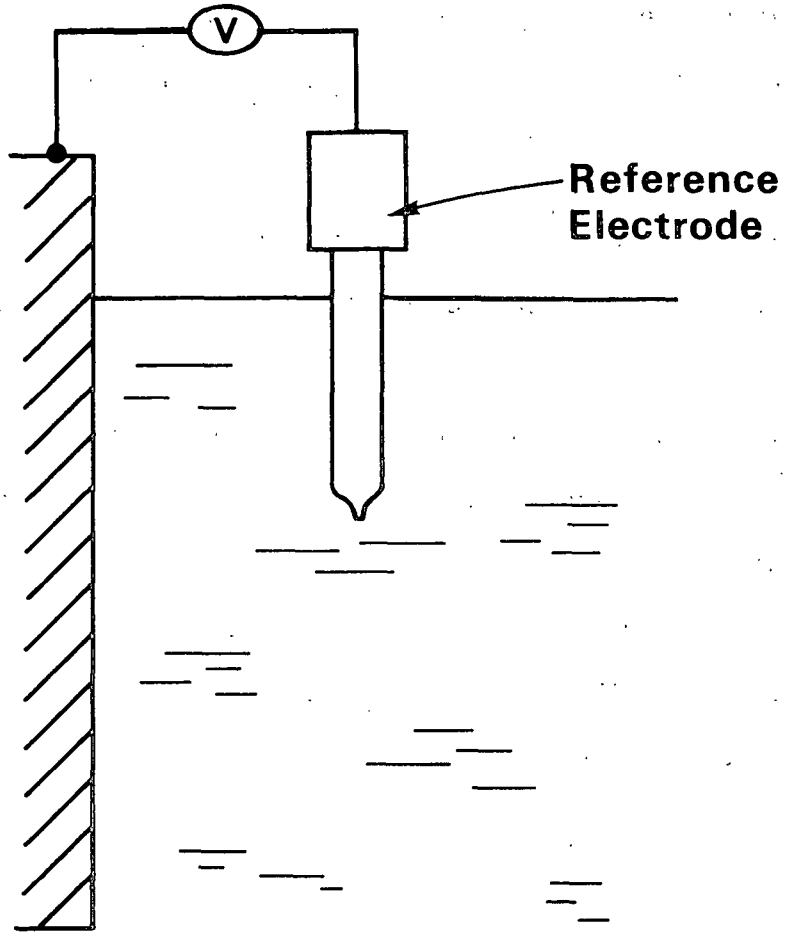


Figure 23. Measurement of potential at a metal/electrolyte interface.

The voltage at the metal/electrolyte interface can influence the rate of the oxidation or reduction reactions occurring at anode or cathode (respectively) sites on a metal surface. If the metal is connected to a sink for electrons —— for example, the positive (+) terminal of a battery —— the rate of oxidation will increase and the rate of reduction will decrease, with the battery consuming the excess electrons produced by the imbalance between oxidation and reduction. If the

voltage is decreased by reversing leads to the battery, the reduction reaction will be favored over the oxidation reaction, and the battery will act as a source of electrons at its negative (-) terminal. Changing the voltage developed at a metal/electrolyte interface is called polarization, with anodic polarization defined as an increase in voltage and cathodic polarization defined as a decrease in the voltage.

If the voltage across the metal electrolyte interface is raised by more than about 75 mV, the oxidation reaction will occur more rapidly but the reduction reaction will virtually stop. All of the electrons created by the oxidation will be consumed by the battery acting as an electron sink. Under these conditions, a linear relationship is often found between the magnitude of applied voltage and the logarithm of the oxidation (i.e., anodic) current as shown in Fig. 24. Current, I, is usually expressed as a current density, i, by dividing the total current by the surface area of the metal. Then, the voltage change, $E-E_{corr}$, is proportional to the logarithm of the current density, i, as follows

$$E-E_{corr} = A + \beta'_a \log i_a \qquad (15)$$

The constant of proportionality between the voltage displacement and the logarithm of the current density is called the anodic Tafel constant, β'_a.

A similar situation prevails when the voltage at the metal/electrolyte interface is artificially displaced to lower potentials. In this case, the constant of proportionality is the cathodic Tafel constant, β'_c

$$E_{corr}-E = C + \beta'_c \log i_c \qquad (16)$$

as shown in Fig. 25.

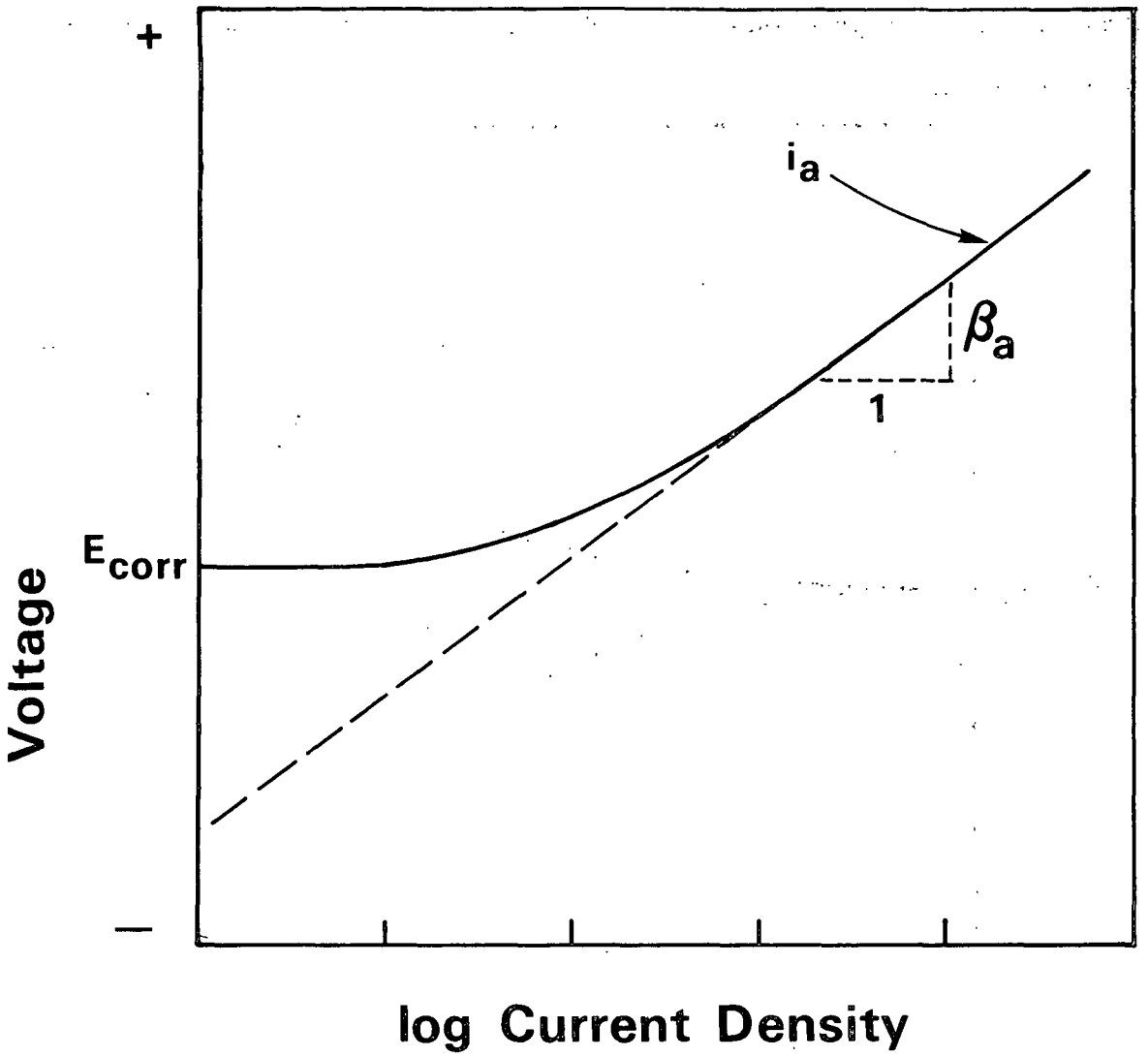


Figure 24. Anodic polarization curve showing the linear relationship between applied voltage and the logarithm of the applied current for polarizations of large magnitude.

The open circuit potential (or corrosion potential, E_{corr}) is the potential where the anodic and cathodic currents are equal. From Fig. 25, it is seen that extrapolations of the straight-line portions of the anodic and cathodic curves intersect at the corrosion potential. The current density at which this occurs is the corrosion current density, i_{corr}. The value of i_{corr} is the total electron current created by all anodic dissolution processes [e.g., Eq. (12)] and consumed by

the cathodic reduction processes [e.g., Eq. (13) or (14)] when no artificial potential is maintained.

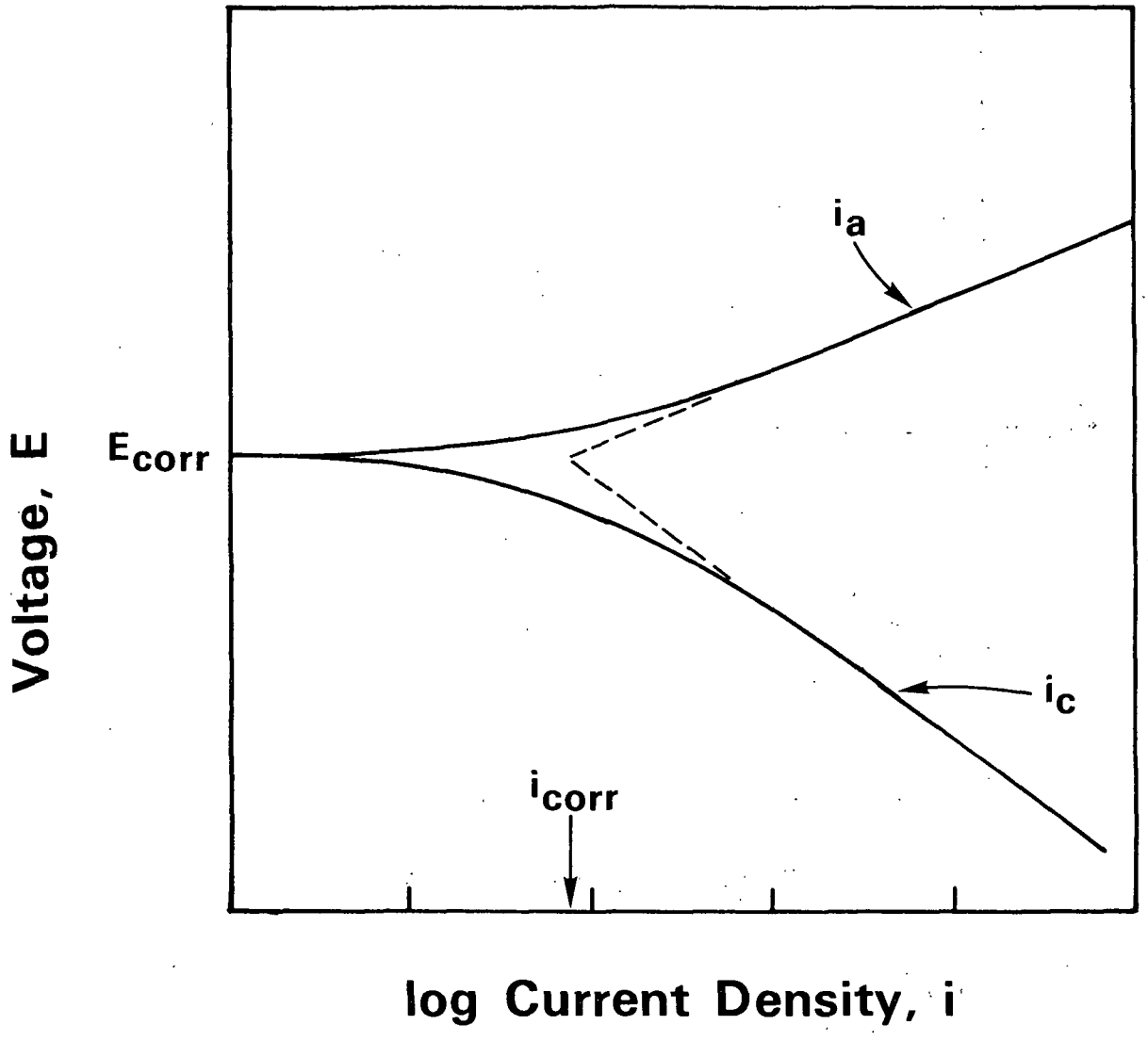


Figure 25. Anodic and cathodic polarization curves showing Tafel behavior. The open circuit potential is determined vs. the potential where $i_a = i_c = i_{corr}$, as indicated by extrapolations of β_a and β_c.

The corrosion current density, i_{corr}, is proportional to the rate of metal loss (length removed/time) at the rest potential, E_{corr}, as given by Faraday's Law.

$$\text{Corrosion Rate} = \frac{(i_{corr})\ (MW)}{F\ (Z)\ (\rho)} \qquad (17)$$

where MW = molecular weight of metal

ρ = density of metal

F = Faradays constant $\cong 96{,}500 \frac{\text{Amp-sec}}{\text{mole}}$

and Z = oxidation number of the ion product created by corrosion.

For corrosion of iron via Eq. (12), Z = 2, MW = 55.85 g/mole and ρ = 7.87 g/cm^3. If the corrosion current density, i_{corr}, is given in mA/cm^2, and the corrosion rate, CR, in mils per year,

$$CR \cong i_{corr}\ (460)\ \text{mpy}$$

If either of the Tafel slopes can be accurately determined, extrapolation of the Tafel (or straight-line) portion of the polarization curve to E_{corr} will yield a value for i_{corr} that can be used in Eq. (17) to calculate the corrosion rate. An example of this Tafel slope extrapolation method is shown in Fig. 25. This Tafel slope extrapolation method is accurate, but cannot be used when the straight-line portions of the polarization curves are too short to allow accurate extrapolation, as in Fig. 26. Moreover, the large excursions in potential necessary to determine the Tafel constants can disrupt the normal corrosion behavior and give erroneous results in subsequent measurements.

The linear polarization method avoids these problems by employing small changes in potential to characterize the corrosion behavior. In the vicinity of E_{corr} —— within perhaps ± 10 mV of E_{corr}, for example —— there is a linear, not logarithmic, relationship between the polarization ($E-E_{corr}$) and applied current density, i. The ratio of ($E-E_{corr}$) and i is a resistance, R, and the corrosion current i_{corr} is inversely proportional to this resistance ...

$$i_{corr} = K\ (1/R) \qquad (18)$$

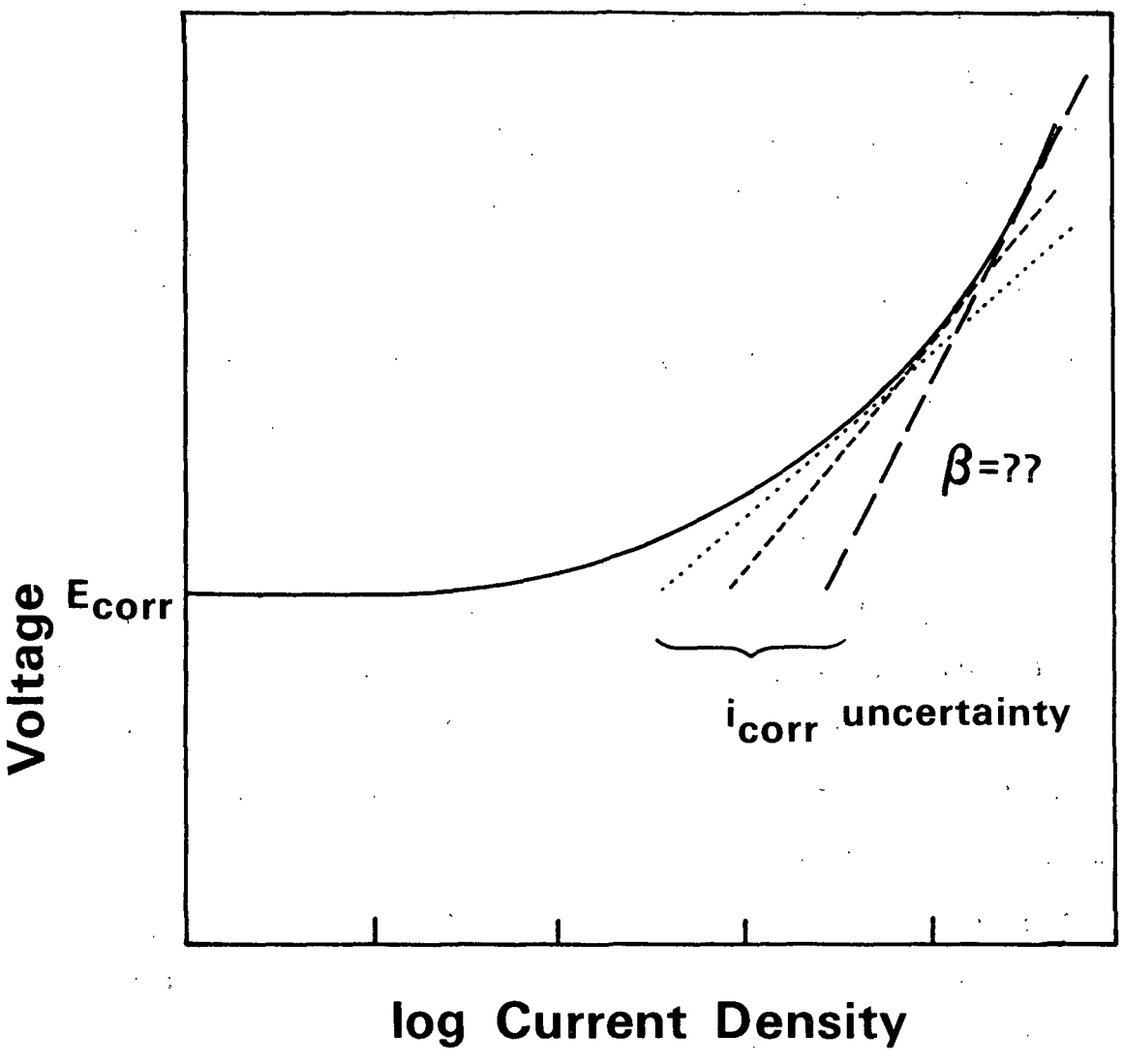


Figure 26. Errors in estimation of i_{corr} due to a nonlinearity in the $(E-E_{corr})$ vs. log i plot.

The constant of proportionality, K, in Eq. (18) can be derived as follows. As shown in Fig. 27 the applied current density, $i_{applied}$, is the difference between the anodic and cathodic current density,

$$i_{applied} = i_a - i_c \qquad (19)$$

The anodic current is given by Eq. (15), which can be reformulated as

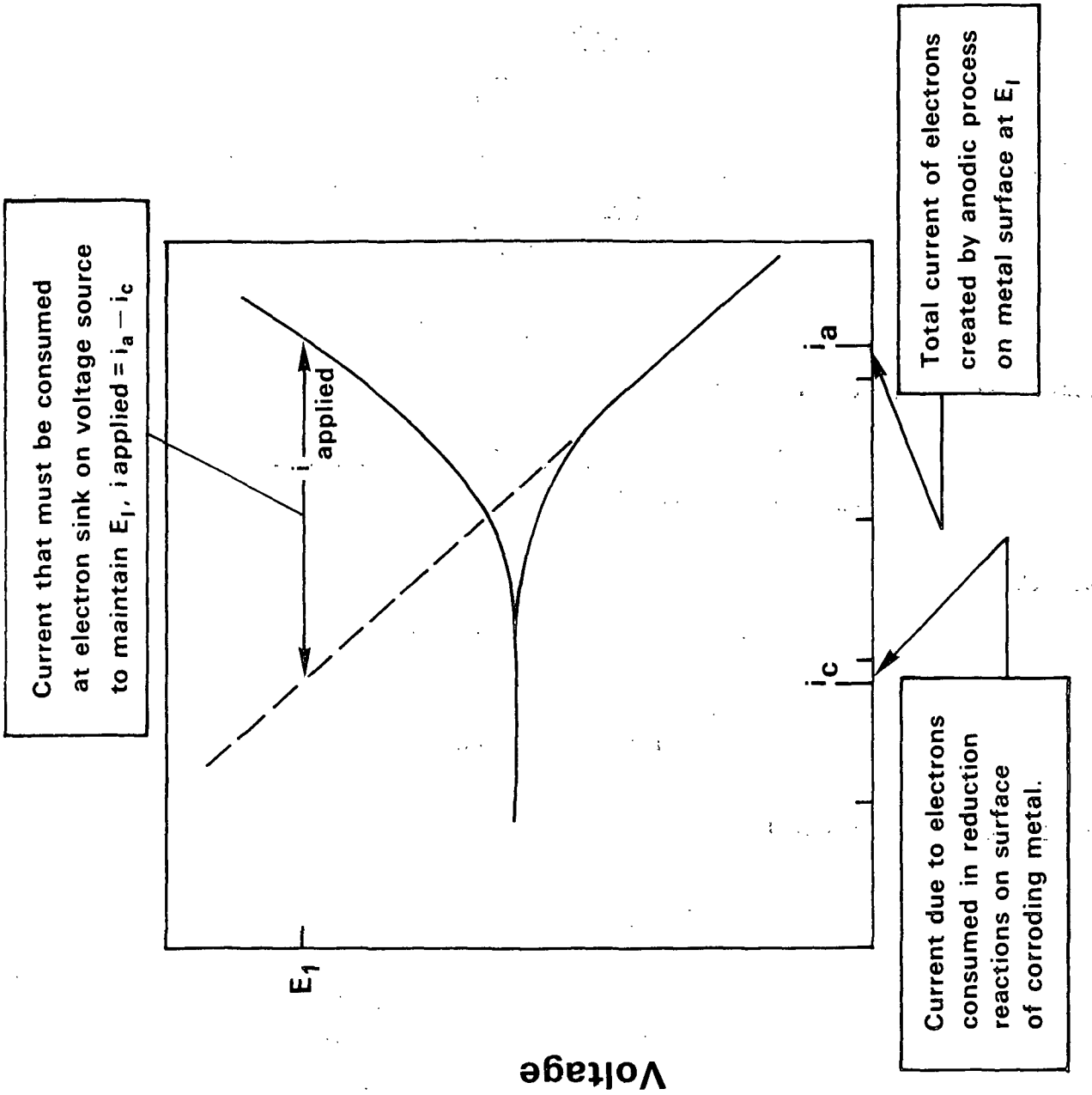


Figure 27. Schematic illustration of the current consumed by the voltage source holding voltage, E_1.

$$E - E_{corr} = \beta_a \log \left(\frac{i_a}{i_{corr}}\right) \tag{20}$$

or

$$10^{\left(\frac{E-E_{corr}}{\beta_a}\right)} = \frac{i_a}{i_{corr}} \tag{21}$$

Similarly,

$$10^{\left(\frac{-E+E_{corr}}{\beta_c}\right)} = \frac{i_c}{i_{corr}} \tag{22}$$

Substituting in Eq. (19), we get

$$i_{applied} = i_{corr} \left[10^{\left(\frac{E-E_{corr}}{\beta_a}\right)} - 10^{-\left(\frac{E-E_{corr}}{\beta_c}\right)}\right]$$

Recall that

$$10^x = 1 + 2.3x + \frac{2.3\ x^2}{2!} + \ldots$$

$$\approx 1 + 2.3x \text{ for small } x.$$

Then, if $(E-E_{corr})$ is small,

$$i_{applied} = i_{corr} \left[2.3\ (E-E_{corr})\ \left(\frac{1}{\beta_a} + \frac{1}{\beta_c}\right)\right]$$

$$= i_{corr} \left[2.3\ (E-E_{corr})\ \left(\frac{\beta_a + \beta_c}{\beta_a \beta_c}\right)\right]$$

And,

$$i_{corr} = \left(\frac{i_{applied}}{E-E_{corr}}\right) \left(\frac{1}{2.3}\right) \left(\frac{\beta_a \beta_c}{\beta_a + \beta_c}\right) \tag{23}$$

$$= \left(\frac{1}{2.3R}\right) \left(\frac{\beta_a \beta_c}{\beta_a + \beta_c}\right)$$

This relationship says that i_{corr} is determined if β_a, β_c, and R are known. R is determined by plotting $i_{applied}$ vs. $(E-E_{corr})$ and determining the slope, R, as shown in Fig. 28. The constants β_a and β_c must be determined independently from polarization curves or must be approximated.

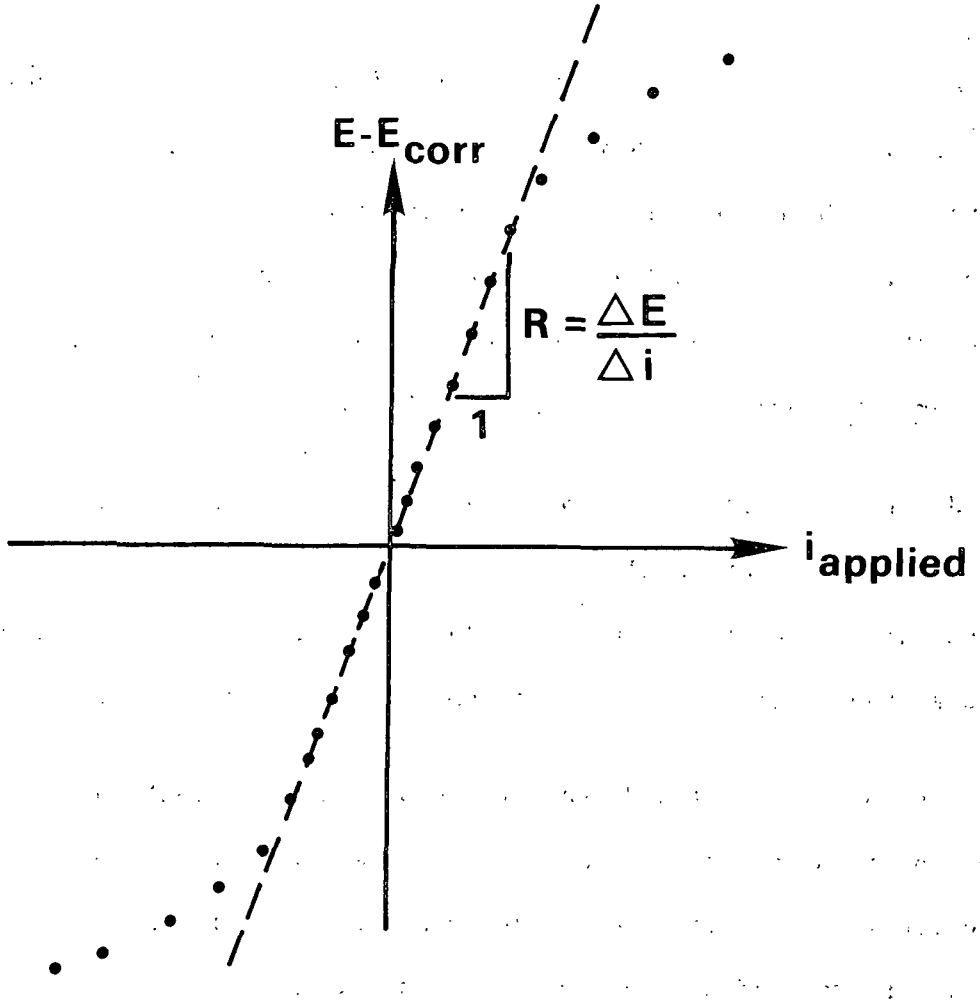


Figure 28. Estimation of polarization resistance, R, from the slopes of the $i_{applied}$ vs. $(E-E_{corr})$ plot.

The linear polarization method depends on the values of β_a and β_c, so determination of these values is critical to the accuracy of the method. Obviously, if the values of β_a and β_c are not obtainable for the Tafel slope extrapolation, they will also not be available for the linear polarization equation. However, the

linear polarization method is less affected by uncertainty in the values of β_a and β_c for two reasons. First, the β's appear as a ratio in the expression

$$\beta = \frac{\beta_a \beta_c}{\beta_a + \beta_c} \qquad (24)$$

which is not a sensitive function of changes in β'_a and β'_c in the ranges encountered in practice. A crude approximation of i_{corr} can be obtained by assuming that β_a and β_c are both 100 mV/decade. Second, even if the β constant cannot be determined independently, the constant K in Eq. (18) can be determined empirically by comparing the actual corrosion rate and the rate measured by linear polarization methods and thereafter using the empirical calibration factor.

An advantage of the Linear Polarization method is that the potentials imposed on a metal sample are small, on the order of 10 mV, and this small perturbation does not alter the corrosion rate. An additional advantage of the LP method is that it is suitable for automated measurements using simple instrumentation.

In fact, several unstated assumptions are also inherent in the derivation of the linear polarization equation described above. One assumption is that the rate of corrosion is not controlled by processes such as diffusion of species to or from the metal surface. If this assumption is not valid, the apparent values of β_a and β_c must be determined empirically by weight loss measurements. Similarly, it is assumed that passivation has not occurred on the electrode surfaces because of an effect on the values of R and β.

A more detailed description of the linear polarization method and its application in corrosion rate measurements is found in review articles by Mansfeld (3) and Barnartt (21).